MERCURY IN ARCTIC SNOW: FACTORS AFFECTING THE KINETICS OF PHOTOREACTIONS

by

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ABSTRACT

Mercury (Hg) is a ubiquitous and toxic environmental contaminant. Hg is problematic in Arctic regions, where organisms accumulate high contaminant levels, and changing climate conditions may alter Hg dynamics in unpredictable ways. This thesis quantified the effects of ultraviolet radiation (UV; 280 – 400 nm) intensity, snow temperature, and chloride (Cl^-) concentration on Hg photoreaction kinetics in Arctic snow, using controlled laboratory experiments and an Arctic field flux campaign. In the first study, photoreduced Hg amounts ($Hg(II)_{red}$) were found to increase with UV intensity for snow from three Arctic sites, while photoreduction rate constants (*k*) had a parabolic relationship with UV. Photooxidized Hg amounts ($Hg(0)_{ox}$) differed at these three Arctic sites, with the greatest photooxidation occurring at the site with the highest Cl^- concentration. The second laboratory experiments determined that increasing temperatures (-20 to -2°C) with constant UV irradiation does not significantly alter Hg photoreduction kinetics, until snow melts (above -5 °C). From a field flux study and generalised additive model analysis, both temperature and snow age have statistically significant influences on Hg(0) flux from snow. Cross correlation analysis found that changes in Hg(0) flux lag temperature by ~30 min, implying that temperature does not have an immediate effect on Hg(0) flux, and so likely does not directly affect Hg photoreaction kinetics. In contrast, Hg(0) flux lags UV radiation changes by only ~5 min, implying that UV changes result in near immediate Hg(0) flux changes, and is directly influencing Hg reaction kinetics. The third laboratory study concluded that increasing Cl^- decreases $Hg(II)_{red}$ in melted Arctic snow, while *k* increases. When both UV and Cl^- vary, it is changing Cl^- that controls *k*,

but both are important for determining $Hg(II)_{red}$. Overall, this work shows that greater emphasis should be placed on examining cryospheric Hg dynamics in the changing Arctic environment. Changing conditions will mean greater Cl^- loading to coastal snow, with an earlier onset of snowmelt (exposure to different intensities of UV pre and post melt), and higher temperatures earlier in the season, and these factors will affect the rate (k) and extent ($Hg(II)_{red}$) of Hg photoreactions in Arctic snow.

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LIST OF ABBREVIATIONS AND SYMBOLS

ACIA = Arctic Climate Impact Assessment

AMAP = Arctic Monitoring and Assessment Program

AMDE(s) = Atmospheric mercury depletion event(s)

$Br^{\bullet}$ = Bromine radical

BrCl = Bromine monochloride

$BrO^{\bullet}$ = Bromine oxide radical

Cl^{-} = Chloride ion

$Cl^{\bullet}$ = Chlorine radical

$ClO^{\bullet}$ = Chlorine oxide radical

CRC = Canada Research Chair

CREATE = Collaborative Research and Training Experience

CSE = Chloride stabilisation effect

CVAFS = Cold vapor atomic fluorescence spectrometer/spectrometry

DOC = Dissolved organic carbon

DOM = Dissolved organic matter

EMEP = European Monitoring and Evaluation Programme

ERM = Easily reducible mercury

Fe = Iron

Fe(II) = Ferrous iron; Fe^{2+} ion

Fe(III) = Ferric iron; Fe^{3+} ion

Fig. = Figure

GAM = Generalised additive model

GEM = Gaseous elemental mercury

GMOS = Global Mercury Observation System

GRAHM = Global/Regional Heavy Metals Model

H_2O_2 = Hydrogen peroxide

HCl = Hydrochloric acid

HDPE = High density polyethylene

Hg = Mercury

Hg(0) = Elemental mercury

$Hg(0)_{ox}$ = Photooxidized mercury amount

Hg(I) = Hg_2^{2+} ion

Hg(II) = Divalent mercury, also referred to as inorganic mercury; the Hg^{2+} ion

$Hg(II)_{red}$ = (Total) photoreduced mercury amount

$Hg(II)_{red,0}$ = The amount of photoreducible Hg in the absence of UV radiation

HNO_3 = Nitric acid

$HO_2^{\cdot}$ = Hydroperoxy radical

IPCC = Intergovernmental Panel on Climate Change

IUV = The intensity of UV radiation an experimental sample was exposed to ($W \cdot m^{-2}$)

k = Pseudo-first order mercury photoreduction rate constant

k_{ox} = Pseudo-first order mercury oxidation rate constant

MDN = Mercury Deposition Network

MeHg = Monomethylmercury ion $(CH_3)Hg^+$

NaCl = Sodium chloride

NS = Nova Scotia

NSERC = National Science and Engineering Research Council

NU = Nunavut

$^{\cdot}OH$ = Hydroxyl radical

PHg = Particle bound mercury

PM = Particulate matter

PTFE = WHAT, also known as Teflon

QLL = Quasi-liquid layer

RGM = Reactive gaseous mercury

SIA = Snow interstitial air

THg = Total mercury

UNEP = United Nations Environment Program

US = United States

US EPA = United States Environmental Protection Agency

UV = Ultraviolet

UVA = Ultraviolet A

UVB = Ultraviolet B

LIST OF APPENDICES

CHAPTER 1: OVERVIEW

1 Global Mercury Distribution

Mercury (Hg) is a neurotoxic and bioaccumulative environmental contaminant found all over the world. Some regions, like the Arctic, are isolated from a great deal of direct point source Hg contamination, but will still receive Hg from natural and anthropogenic emission sources through long range atmospheric transport as a result of the long atmospheric lifetime of Hg (0.5 to 2 years) (Selin et al., 2008).

Naturally-emitted Hg occurs primarily as elemental mercury (Hg(0)) (Ryaboshapko et al., 2007), while anthropogenic Hg emissions can occur as Hg(0), divalent Hg (Hg(II)) or methylmercury (MeHg) species, however only Hg(0) will undergo long range atmospheric transport, since MeHg and Hg(II) have short atmospheric lifetimes (Keeler et al., 2005; Lin and Pehkonen, 1999; Schroeder et al., 1998). Once deposited to Earth's surface, Hg can undergo many reactions, changing speciation and potentially allowing re-emission back to the atmosphere. This means that while emission sources provide Hg to remote locations, ultimately *in situ* reactions will determine speciation and extent of Hg re-emission from surface environments, and so the magnitude of surface Hg contamination. This makes characterisation of these *in situ* Hg reactions, their kinetics, and the factors affecting these kinetics of critical importance to expressing the dynamics of Hg in remote environments.

2 Arctic Mercury

Mercury (Hg) is of particular concern to Arctic environments, as organisms therein tend to accumulate high levels of Hg, which can be passed on to humans who rely on these food sources as a part of their traditional lifestyle (Ford 2009; Carrie et al. 2010; Kirk et al. 2012). The Arctic is a remote environment and so does not have major local sources of anthropogenic Hg contamination, but rather Hg moves to the Arctic by long range atmospheric or oceanic transport (Durnford et al., 2010; Slemr et al., 2003). Falling snow represents an important way for Hg to move to surface environments; however, Hg in snow is very labile (Lalonde et al., 2002; Poissant et al., 2008; Schroeder and Munthe, 1998), changing speciation and undergoing dynamic exchange with the atmosphere. Photochemical reactions are the main way that Hg is lost from snow prior to the melt period (Lalonde et al., 2002, 2001), when ions, such as Hg(II), are flushed from the snowpack with the first fractions of melt water (Dommergue et al., 2010; Kuhn, 2001). Hg photochemical reactions, namely photooxidation and photoreduction, occur in the sunlit portion of the snowpack. These reactions transform Hg between oxidized forms (Hg(II)) that are retained in the snowpack, and reduced Hg (Hg(0)) which can be lost to the atmosphere. Loss of Hg(0) from snow can occur through snowpack ventilation processes (Ferrari et al., 2005) and/or diffusion, or movement with concentration/temperature gradients (Albert and Shultz, 2002; Anderson and Neff, 2008; Kuhn, 2001), since ice surfaces do not bind Hg(0) effectively (Bartels-Rausch et al., 2008; Ferrari et al., 2004). The balance of these photoreactions will thus control how

much Hg will remain in a snowpack until melt, and so determine how much Hg can move into receiving water bodies where it has the potential to enter food webs.

Changes in the Arctic climate have the potential to influence these important snowpack Hg photochemical reactions. In particular, temperatures are predicted to increase (ACIA, 2005), which may affect Hg photoreaction kinetics directly or in indirect ways. Higher temperatures will lead to an earlier onset of melt (ACIA, 2005), which means snow will be exposed to different intensities of UV radiation both before and after it melts. In addition, higher temperatures lead to more open water in the Arctic Ocean year round (ACIA, 2005), which has the potential to deliver more chloride to snow near this open water, since most of the chloride found in coastal snow comes from sea salt aerosol (Krnavek et al., 2012). Snowpack temperature, UV radiation intensity, and chloride concentration have all been proposed to directly influence the kinetics of Hg photochemical reactions in Arctic snow (Durnford and Dastoor, 2011); however, a quantitative understanding of their effects on Hg photoreactions is presently absent, making scientists unable to reliably predict the effects of the changing Arctic climate on Hg dynamics.

3 Thesis rationale

Quantifying the rate of Hg photooxidation and photoreduction reactions and the extent to which Hg is transformed between species is key to an accurate description of Hg cycling in the cryosphere. In addition, quantifying these kinetics is essential to predicting the extent of Hg transport with melt water, since photoredox reactions largely control the

post-depositional fate of Hg in snow. Environmental factors like temperature, radiation intensity, and chemical composition of the snow (specifically chloride concentration), among others have been proposed to influence Hg photoreduction and/or photooxidation reactions (Durnford and Dastoor, 2011). Unfortunately, snow is a very complex medium, composed of air, liquid and solid water, and particles, where the ratio of these different components will change with time, temperature, and subsequent snowfall. In addition, contaminants can exhibit different reactivity depending on their phase association. Due to the complexity and changeable nature of snow, it is difficult to quantify the influence of individual environmental factors on snowpack Hg photoreactions, since many factors could be changing at the same time, confounding efforts to predict Hg photoreactions in a changing Arctic environment.

The general objective of the work presented in this thesis was to quantify the effects of UV radiation intensity, snow pack temperature and chloride concentration on the rate and extent of Hg photoreactions in Arctic frozen and/or melted snow. By performing experiments in the controlled environment of the laboratory, it was possible to isolate these factors (UV intensity, temperature, and chloride concentration) and vary them independently, thereby allowing quantification of the influence of each factor on Hg photoreduction kinetics, without being forced to rely strictly on natural environmental variability. The determination of Hg photoreaction kinetics based on each of the isolated variables allows for better future prediction of Hg dynamics in the changing Arctic environment, specifically providing much needed kinetic parameters that can be used in current and future predictive models. The results collected in this work represent the first

of their kind Hg photoreaction kinetic measurements relative to single environmental variables, and fill a critical gap in the present understanding of Hg dynamics in Arctic snow.

Snow was collected from Resolute Bay, NU, Canada in March 2012 and 2013, and from Alert, NU, Canada in May 2014. These samples were shipped back to the O'Driscoll lab at Acadia University in Wolfville, NS, Canada where analyses were performed to determine the kinetics of Hg photoredox reactions in frozen and/or melted snow relative to UV intensity, temperature and added chloride concentration in 2012, 2013 and 2014 respectively. A controlled laboratory set up was used for these studies and each factor (UV intensity, temperature and added chloride concentration) was modified individually, thereby removing many of the confounding variations seen in field studies and allowing determination of the influence of each factor on Hg photoreduction kinetics. In addition one *in situ* field flux study was performed in 2013 to determine the effect of temperature, UV intensity and snow age on the magnitude of Hg(0) flux from snow in the complex native environment. From this *in situ* study, mechanistic information was derived about the influence of UV intensity and temperature on Hg(0) flux from Arctic snow.

4 Thesis organisation

This thesis consists of six chapters, the first and last chapters are the overview and summary, respectively. Chapter two is a literature review looking at cryospheric Hg, the factors affecting Hg cycling in snow and ends with an examination of existing knowledge

gaps, which provided the impetus for the studies enumerated in chapters three to five. Chapters three through five are presented as individual research papers related to three sets of experiments, and each chapter has its own introduction and conclusions. As a result of this structure, the overview and summary chapters (chapter 1 and 6) have been kept intentionally short in an effort to reduce redundancy, with the main conclusions of chapters three through five presented in the summary (chapter 6). The hypotheses for chapters three through five have been provided below.

Chapter three examines the influence of UV radiation on the kinetics of Hg photoreduction and photooxidation in melted Arctic snow, and photoreduction in frozen Arctic snow. It was hypothesized that a statistically significant relationship could be derived between the intensity of UV radiation received by a frozen and/or melted snow sample and the pseudo-first order photoreduction rate constant (k) and the total photoreduced Hg amount ($Hg(II)_{red}$). It was further hypothesized that Hg photoreduction and photooxidation kinetics would differ in snow sampled from three discrete Arctic sites as a result of differences in the chemical composition of the snow, specifically ions like chloride.

The experimental study described in chapter four aimed to further investigate the influence of environmental variables on the kinetics of Hg photoreduction by hypothesizing that temperature influences Hg photoreduction kinetics in frozen Arctic snow. In this chapter, a field study is also described. In this field study, it was hypothesized that older Arctic snow would produce smaller Hg(0) emission fluxes, since

photoreducible Hg in snow is expected to be a discrete pool, and so with time the Hg that can be photoreduced will be depleted, unless Hg is added via wet or dry deposition.

The work described in chapter five builds directly on the conclusions of chapter three, namely the conclusion that differences in snowpack chemical composition (i.e. chloride concentration) may lead to differences in Hg photoreduction kinetics. In this work, the influence of chloride concentration on the kinetics of Hg photoreduction in melted Arctic snow was studied. It was hypothesized that higher chloride concentrations would reduce the amount of Hg in a sample that could be photoreduced and alter the rate constant of that Hg photoreduction in melted Arctic snow.

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CO-AUTHORSHIP STATEMENT

The initial idea for the project was proposed by Dr. Nelson O'Driscoll, in response to my interest in continuing research on both snow and mercury with him. The idea for the first experimental study (mercury photoreactions as related to ultraviolet radiation intensity) was proposed by Dr. O'Driscoll, while the particulars of the study were designed by myself, and then discussed during a meeting of the full supervisory committee prior to the first field campaign. Experimental studies two (mercury field flux and the dependence of reactions on temperature) and three (the dependence of mercury photoreaction kinetics on chloride concentration) were initially proposed by myself, with the support and assistance of Dr. O'Driscoll as natural extensions of results determined in the first experimental study, and knowledge gaps found in the literature. Ideas were all put to supervisory committee. From such meetings, the field campaigns and experimental designs were fleshed out and experiments undertaken. Determination of the practical scale for each of the three experimental studies enumerated in this thesis was assisted by all members of my supervisory committee, with the first experiment requiring the most guidance in terms of the reasonable scale of the research to be completed. Field and laboratory experimental designs were put forth by myself, with suggestions and comments provided by all committee members.

The practical aspects of the research were performed by myself, under the direct supervision of Dr. Nelson O'Driscoll, and the remote supervision of Dr. Susan Ziegler. I designed field campaigns for sample acquisition and data collection in 2012 and 2013, and I performed data collection, with Dr. Mark Mallory in 2012 and Dr. Mark Mallory

and Dr. Nelson O'Driscoll in 2013 assisting with the field campaigns and field data collection in Resolute Bay, NU, Canada. I undertook the laboratory analyses to acquire the results presented in this thesis, with help from John Dalziel and Rob Tordon of Environment Canada for instrumental issues. In addition, results were discussed with all members of my supervisory committee, and Dr. Trevor Avery provided assistance for statistical analyses. Full committee meetings were regularly held to discuss the findings, and comments/suggestion were provided by the various members.

I prepared the initial manuscripts following the completion of the data collection and analysis, with initial planning and organisation of the manuscripts assisted by Dr. O'Driscoll. Suggested revisions, comments and edits were provided by all coauthors for each manuscript making up this thesis and the anonymous reviewers for the manuscripts making up chapters two and three. I integrated these into the papers submitted for publication, and those that have yet to be published, and compiled these manuscripts into the presented thesis.

CHAPTER 2: MERCURY PHOTOCHEMISTRY IN SNOW AND IMPLICATIONS FOR ARCTIC ECOSYSTEMS

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Abstract

Mercury is a toxic and bioaccumulative environmental contaminant, which may be transported to remote regions around the world such as the Arctic. Snow melt is a major source of mercury to many surface water environments, but the amount of mercury in snow varies considerably. This variation is due to the balance of mercury retention and losses from snow, which is largely controlled by photochemical mechanisms controlling speciation. As such, quantifying these photochemical reaction rates and the factors affecting them will allow for the prediction of mercury speciation and movement into receiving water bodies. This will consequently improve our ability to predict exposure of aquatic organisms to mercury. This review highlights knowledge gaps in the quantification of mercury photochemical kinetics and the specific research required to advance the science of mercury photochemistry in snow, by examining the physical and chemical snowpack variables that influence snowpack mercury reactions. At present, our lack of mechanistic and kinetic knowledge of mercury reactions in snow is one of the greatest gaps preventing accurate predictions of mercury fate in regions containing seasonal snowpacks.

1 Introduction

Mercury (Hg) is an environmental contaminant of significant concern because it is a neurotoxin with the ability to bioaccumulate and biomagnify (Chang and Hartmann, 1972; Hammerschmidt et al., 2002), and is subject to long range transport, resulting in contamination of remote environments (Slemr et al., 2003). Hg undergoes many

chemical, photochemical and biological reactions which affect its speciation and fate. The formation of methylmercury (MeHg) in particular is of concern since this is the most toxic and bioaccumulative form (Ekino et al., 2007). However, predictions of MeHg formation require reliable estimates of Hg inputs in different environments. Atmospheric deposition has been proposed to be the main source of Hg entering the Arctic Ocean (Mason et al., 1994; Nriagu and Pacyna, 1988; Outridge et al., 2008), where it may subsequently enter the food web, although riverine inputs and ocean currents may also contribute (AMAP, 2011; Fisher et al., 2012; Outridge et al., 2008). In contrast, snowmelt is a primary source of Hg to Arctic wetland systems (Bishop et al., 1995; Demers et al., 2010; Dommergue et al., 2010; Loseto et al., 2004a; Mitchell et al., 2008; Schelker et al., 2011; Schuster et al., 2008). To predict Hg movements with snowmelt, knowledge of the behaviour of the various species of Hg in snow is necessary.

1.1 Mercury speciation

Mercury (Hg) exists in three main environmentally important forms: elemental, divalent, and methylmercury (Schroeder and Munthe, 1998; Steffen et al., 2008). Elemental Hg (Hg(0)) is volatile and exists primarily in the gas phase, either in the atmosphere, or in air pore spaces of soils and snow (O'Driscoll et al., 2005). Divalent Hg (Hg(II)) is the form most prevalent in condensed phases and can be found associated with atmospheric particles, dissolved in water, including snow and ice melt water (O'Driscoll et al., 2008), and associated with solid or liquid phases in soils, sediments and snow (Bartels-Rausch et al., 2011; Ferrari et al., 2005). In the atmosphere, gas phase Hg(II) is

thought to comprise a large portion of the operationally-defined reactive gaseous Hg (RGM) (Brooks et al., 2006; Landis et al., 2002; Lin and Pehkonen, 1999; Stratton et al., 2001), but constitutes a small fraction of total atmospheric Hg (~3%) (Lindberg and Stratton, 1998; Stratton et al., 2001). Nonetheless, this fraction is subject to change, with some areas/times, having higher or lower RGM levels (Cobbett et al., 2007; Steffen et al., 2008). Operationally-defined, particle bound Hg (PHg) is also thought to be Hg(II) (Lin and Pehkonen, 1999) and represents <3% of total atmospheric Hg (Lindberg and Stratton, 1998; Stratton et al., 2001). Methylmercury (MeHg), or the monomethylmercury ion ($HgCH_3(I)$) is the bioaccumulative and neurotoxic form of Hg, and the predominant form found in organisms (Lindberg et al., 2002; Morel et al., 1998). MeHg is also found in natural waters and sediments (Ramlal et al., 1993), and is formed from the anaerobic methylation of Hg(II) (Mason and Sheu, 2002) primarily by sulfate-reducing bacteria in aquatic systems. Sulfate-reducing bacteria methylate Hg(II) as a by-product of microbial respiration (Choi et al., 1994; Choi and Bartha, 1993; Gilmour and Henry, 1991). The most efficient methylation occurs at oxic-anoxic interfaces (Hintelmann et al., 2000). Newly deposited Hg(II) is more reactive in aquatic systems and more likely to be methylated (Hintelmann et al., 2002; Lindberg et al., 2002); thus it is important to quantify Hg(II) inputs to ecosystems in order to better constrain the potential for Hg contamination in the food web. Snowfall and snowmelt are important but poorly constrained Hg(II) inputs to aquatic ecosystems.

1.2 Mercury deposition to snow

As snow falls, it scavenges atmospheric contaminants like Hg, both free in the atmosphere and those sorbed to particles (Ebinghaus et al., 1999; Gardfeldt et al., 2001), depositing them to the ground (Jones, 1999). Additional Hg can be deposited to the snowpack via dry particle or dry gaseous deposition (Cobbett et al., 2007; Fitzgerald et al., 1991). During Arctic spring, large-scale episodic depletion of atmospheric Hg also occurs, during events known as "atmospheric mercury depletion events" (AMDEs) (Ariya et al., 2004, 2002; Schroeder et al., 1998; Steffen et al., 2008). These AMDEs can result in large initial increases in surface snow Hg concentrations as the depleted Hg deposits to the surface (Dommergue et al., 2010), leaving the atmosphere with a characteristically low Hg concentration (Ariya et al., 2004, 2002; Schroeder et al., 1998; Steffen et al., 2008). The overall influence of AMDEs to the total Hg budget of Arctic snow is uncertain, since much of this deposited Hg may quickly be photoreduced and be re-released to the atmosphere (Aspmo et al., 2006; Dommergue et al., 2010; Kirk et al., 2006; Lalonde et al., 2002; Poulain et al., 2004; Sherman et al., 2010; St. Louis et al., 2005), but a significant fraction may also be retained (Ariya et al., 2004; Hirdman et al., 2009; Skov et al., 2004; Steffen et al., 2005).

1.3 The importance of snow

Snow has an important and multifaceted role on the planet. From a climate standpoint, surface snow increases Earth's albedo, thereby reducing surface heating by the sun (Gorodetskaya et al., 2006; Ramanathan et al., 1989; Wang and Zender, 2011).

The water contained in snow is an important hydraulic resource for surface environments (Barnett et al., 2005; Fily et al., 2003). Snow also represents a potential transient sink for contaminants, and a way to transport these contaminants to aquatic or marine ecosystems. Snow crystals are varied, with many different grain shapes and microstructures possible (see Fierz et al. (2009). Even within a relatively small region in the Arctic, different snow types can be found, and these different snow types can have very different Hg concentrations (Douglas et al., 2008). In particular, Arctic snow crystals formed directly from vapour phase water freezing can have up to an order of magnitude more Hg than crystals formed in other ways (Douglas et al., 2008).

Snow is a complex multiphase environmental medium in which contaminants can accumulate and/or undergo chemical or microbial reactions (see review by Larose et al. (2013a)). Hg present in snow is predominantly labile (Lalonde et al., 2002; Poissant et al., 2008; Schroeder and Munthe, 1998), undergoing reactions and changing speciation and phase association (Fig. 2.1). This means that snow is not simply a transient reservoir for cumulative atmospheric Hg inputs, which move into surface waters when snow melts. Since chemical and photochemical reactions can result in a loss of Hg in snow over time (Ferrari et al., 2005; Johnson et al., 2008; Lalonde et al., 2002; Poulain et al., 2004; Steffen et al., 2008), predicting the amount of Hg that will move with melting snow to receiving water bodies requires quantification of the reactions of Hg and the factors influencing those reactions before the melt period.

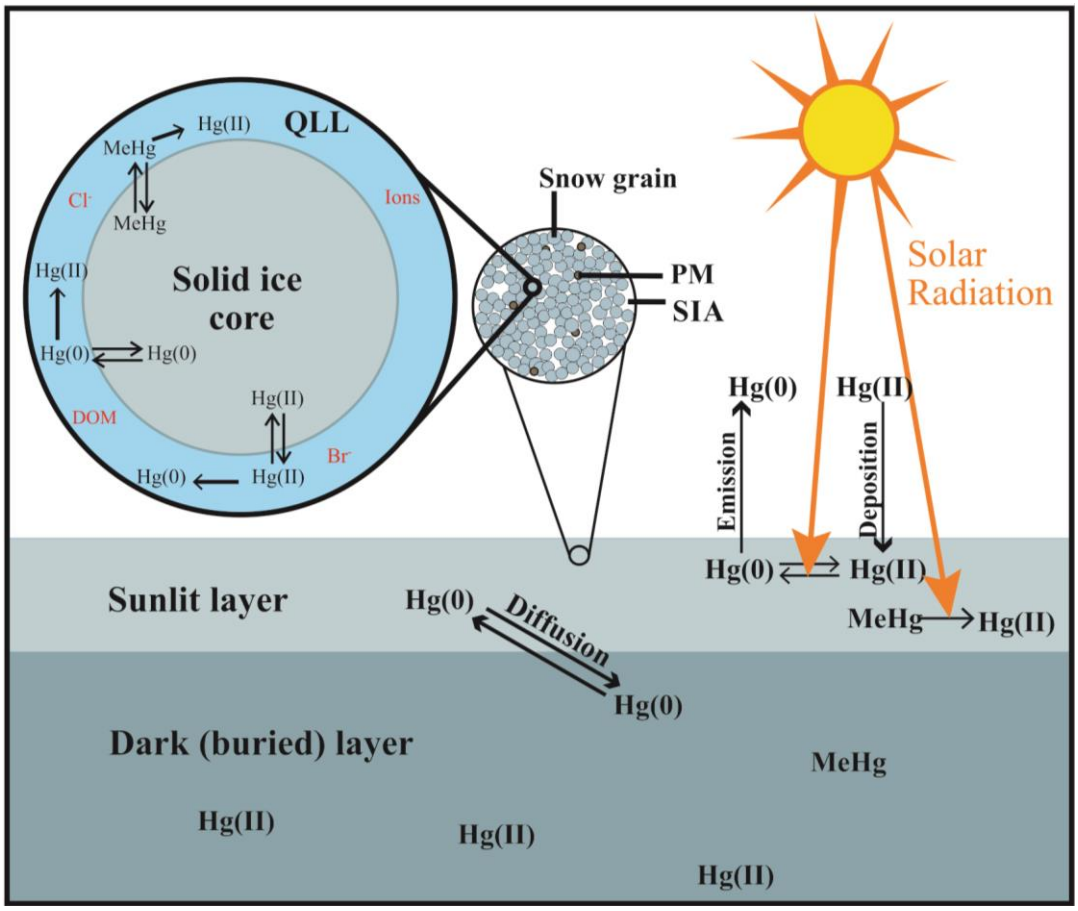

Figure 2.1: The photochemical reactions involved in mercury cycling within a snowpack and between snow and air are shown. Reaction occurs within the sunlit layer of the snowpack, while mercury contained in deeper buried layers is not subject to photochemical reactions. This snow contains snow grains, particulate matter (PM) and snow interstitial air (SIA), and is not necessarily homogeneous. Note that PM is not necessarily associated with the outside of the snow grain, it can be contained within it as well. The quasi-liquid layer (QLL) present around each snow grain has been proposed as the site of reaction, where mercury ions as well as other ionic species, such as halides, and dissolved organic matter (DOM) may influence photochemical reactivity. Movement of chemical species between the solid ice core and the QLL is also possible. Mercury photoreduction within the snowpack will form Hg(0) which may then move from the snowpack through ventilation or diffusion, or be photooxidized back to Hg(II) species. Diffusion of Hg(0) is also possible within and between the snowpack layers. Methylmercury may undergo photodemethylation within the sunlit layer.

Most contaminants enter the Arctic by long range atmospheric or oceanic transport processes (Durnford et al., 2010; Slemr et al., 2003) and not from local point sources (Pacyna and Keeler, 1995), although point source pollution may be becoming more important for Arctic contamination (Steffen et al., 2005). In the spring when snow melts, contaminants remaining in snow after chemical and/or photochemical loss processes can

be transported to wetlands and other aquatic environments (Barrie et al., 1992; Campbell et al., 2005; Fitzgerald et al., 2007; Wagemann et al., 1998). In the case of Hg, transport to aquatic and wetland environments can result in MeHg formation; MeHg can then be bioaccumulated by organisms and biomagnified up the food web (Loseto et al., 2004b). Environmental conditions can influence the rate and extent of snowpack reactions, and so with predicted changes in climate conditions (ACIA, 2005; AMAP, 2011; IPCC, 2013, 2007), it is very likely that the rates of chemical/photochemical reaction or loss processes in snowpacks will change, thereby influencing the potential exposure of aquatic organisms to Hg.

1.4 Forecasted changes in the Arctic snow reservoir

Climate change is predicted to have many effects in the Arctic which may influence Hg fate. Mean annual Arctic precipitation (snow and rain) is predicted to increase by 7.5 – 18% by 2090, with the greatest increases for snowfall in the winter (ACIA, 2005). This increased snowfall could mean greater scavenging of atmospheric contaminants, leading to higher potential Hg deposition to the snowpack, since snow has been found to effectively scavenge both RGM and PHg from the atmosphere (Ariya and Ryzhkov, 2003; Fitzgerald et al., 1991; Lamborg et al., 1995; Lindberg and Stratton, 1998; Lu et al., 2001; Poissant et al., 2008). Additional information can be found in Fisher et al. (2013). Since ~85% of photochemical reactions happen in the top 10 cm of a snowpack (King and Simpson, 2001), greater snowfall could also result in deeper snowpacks, which would reduce the phototransformation of Hg species overall by burying more Hg-

containing snow below the UV penetration depth (Dommergue et al., 2010; Witherow and Lyons, 2008). Mean winter temperatures are predicted to rise 3 – 5 °C by 2090, with faster spring melt and a longer ice-free season (ACIA, 2005). Increasing temperatures and earlier onset melt may result in faster and earlier delivery of Hg in melt water to receiving bodies, like wetlands and the Arctic Ocean, thereby decreasing the time available for snowpack photochemical reactions and loss processes to occur. In addition, the most recent Arctic Monitoring and Assessment Program (AMAP) report (2011) predicted up to a 20% increase in Hg emissions by 2020. Such an increase in emissions could pose a significant risk to ecosystems that efficiently retain and methylate Hg. Collectively, greater Hg emissions and more scavenging with greater snowfall as well as more burial of Hg below the UV penetration depth may result in snowpacks with greater Hg loads, since buried Hg is unavailable for emission (Dommergue et al., 2010; Witherow and Lyons, 2008). Earlier snowmelt onset with higher temperatures may result in faster melt periods and greater masses of Hg delivered to receiving water bodies earlier in the season (Stern et al., 2012). The overlap between peak Hg inputs and peak periods of organism growth and development may result in increased risk to aquatic ecosystems (Stern et al., 2012), since organisms in developmental life stages are more vulnerable to neurotoxic effects (Castoldi et al., 2003; Fjeld et al., 1998; Gilbert and Grant-Webster, 1995).

With future changes in climate, prediction of how much Hg remains to move with melting snow will require determination of the rates of Hg loss in snow due to photochemistry, as well as the effects of environmental factors on these reactions. A

recent review by Durnford and Dastoor (2011) examined the overall behaviour of Hg in the cryosphere. In our current review, we critically examine existing knowledge of the dynamics of Hg photochemical reactions in snow, the factors influencing these reactions, and identify key knowledge gaps where research is required to further the understanding of snow as a source of Hg to natural waters.

2 Mercury photochemistry in snow

Before the melt period, when Hg can move out of a snowpack with melt water (Mann et al., 2011), Hg is lost from snow primarily through photochemical reactions, whether direct or indirect (Lalonde et al., 2002, 2001; O'Driscoll et al., 2006a; O'Driscoll et al., 2005), however dark (chemical) reactions have also been observed (Ferrari et al., 2004b; O'Concubhair et al., 2012). These photochemical reactions will depend on the fate of Hg species in snow, particularly in the context of snowpack physics and transport, and will also be influenced by physical and chemical variables of the snowpack, and the speciation of the Hg itself.

2.1 Snowpack physics and mercury transport

Snow is a complex and dynamic multi-phase environmental medium, containing air, solid particles and water in the solid and liquid phase, where temperature determines the ratio of solid to liquid water. The rate of photoreaction of Hg in snow is different than that in condensed phases (O'Concubhair et al., 2012). Numerous researchers have suggested that the quasi-liquid layer (QLL) of the snow grains is the location of such

photoreactions (Fig. 2.1; (Ferrari et al., 2005; Jacobi et al., 2007; Sherman et al., 2010)) although no experimental evidence of reactions in the QLL has been reported to date.

The quasi-liquid layer (QLL) is a thin, aqueous, liquid-like layer that exists on the surface of all frozen media containing impurities (Jacobi et al., 2007). The thickness of this layer is dependent on snowpack impurities and environmental temperature (Kuo et al., 2011), with warmer temperatures and increased impurities resulting in a thicker QLL (Conde et al., 2008). However, far below the melting point of the bulk snow, such a layer can still exist (Conde et al., 2008; Kuo et al., 2011). When water freezes and molecules form the ice crystal structures that make up snowflakes, the impurities contained therein are excluded from the crystal structures and end up in the QLL surrounding each snowflake (Fig. 2.1), and these impurities may then undergo reaction in the QLL (Colbeck, 1981; Jacobi et al., 2007; Jacobi and Hilker, 2007; Petrenko and Whitworth, 1999). The QLL is not truly liquid, but rather a less organised conglomerate of molecules that behaves like a liquid and provides the location for Hg photoreactions to occur (Faïn et al., 2007). Since reactions in the QLL are primarily surface catalysis processes, the rates of reaction of Hg in snow differ from those seen in the atmosphere (Fain et al., 2006) or in bulk water (O'Concubhair et al., 2012; Schroeder et al., 2003). It is further known that Hg reactions in frozen liquids proceed at faster rates than the same reactions in unfrozen liquids of the same composition (O'Concubhair et al., 2012), which suggests that reactions rates of Hg may be higher in the QLL compared to bulk liquids.

Photochemical reduction of Hg(II) results in Hg(0) formation (Fig. 2.1), but Hg(0) does not sorb effectively to snow crystals (Bartels-Rausch et al., 2008; Ferrari et al.,

2004a). Therefore, much of the Hg(0) formed in the snowpack is easily lost through snowpack ventilation by wind (Ferrari et al., 2005) or diffusion as a result of temperature/concentration gradients (Albert and Shultz, 2002; Anderson and Neff, 2008; Kuhn, 2001), decreasing Hg concentrations in the snow (Fig. 2.1). Wind-driven transport in an Arctic snowpack can move contained volatile species, like Hg(0), from depths up to 50 – 100 cm, though this wind ventilation depth will vary depending on the physical properties of the snowpack (Albert et al., 2002; Albert and Shultz, 2002) and also the chemical properties of the contaminant of interest, which has been reviewed by Domine et al.(2008).

2.2 Reactions and factors influencing mercury photoreactions

Photochemical reduction of Hg has been measured in snow, although kinetic data are relatively scarce and many specific reactions have not been quantified in detail (Fig. 2.2). Dommergue et al. (2007) found that Hg photoreduction reaction rate constants in temperate, alpine and polar snow were 0.25 or 0.18 h^{-1}, using first order kinetics after monitoring the decrease in Hg flux from irradiated snow over time. Poulain et al. (2004) estimated the maximum rate of photoproduction of Hg(0), presumed to be due to Hg(II) photoreduction, in Arctic snow incubated for 3 h under incident solar radiation to be 1.33 $pmol \cdot L^{-1} \cdot h^{-1}$. Poulain et al. (2007b) determined that the rate of photoproduction of Hg(0) in temperate snow was 0.04 $pmol \cdot L^{-1} \cdot h^{-1}$ and 0.27 $pmol \cdot L^{-1} \cdot h^{-1}$, where samples were incubated for 3 h under canopy cover or open sky, respectively. Lalonde et al. (2002) determined the Hg(II) reduction rate in temperate snow incubated under incident solar

radiation was 1.6 $pmol \cdot L^{-1} \cdot h^{-1}$, assuming pseudo-zero order kinetics and photolytic reduction of Hg(II). However in a later paper, Lalonde et al. (2003) determined that Hg(II) reduction in snow is not a direct photolytic process, but is photolytically initiated. Dommergue et al. (2003) found the rate of Hg(0) production at 25 – 54 cm depth in a sub-arctic snowpack to be 0.0006 – 0.002 $pmol \cdot L^{-1} \cdot h^{-1}$ prior to snowmelt, and 0.006 – 0.02 $pmol \cdot L^{-1} \cdot h^{-1}$ at the onset of melt. Determination of these rate values was done under varying environmental conditions, and therefore rates over several orders of magnitude have been reported, as the above studies show. The result is a great deal of uncertainty as to the rate and extent of photochemical reduction of Hg in snow, leading to a poor grasp of the amount of Hg that will remain in an Arctic snowpack at the onset of melt.

While there are a few papers examining Hg photochemical reduction kinetics in snow, there is less known about Hg photochemical oxidation kinetics in snow. It is assumed that Hg(0) oxidation results in the formation of an Hg(II) species, since Hg(I) is typically unstable under environmental conditions, dissociating to Hg(II) (Baltisberger et al., 1979; Schroeder and Munthe, 1998). Lalonde et al. (2003) determined that Hg oxidation can occur in snow by spiking melted Arctic snow with aqueous Hg(0) and quantifying Hg(0) after irradiation, and Poulain et al. (2004) observed a decrease in volatile Hg species in bottles filled with Arctic snow and incubated under the June sun, but no kinetic rates were derived in either case. Fain et al. (2006) gave the rate of gaseous elemental mercury (Hg(0)) depletion in snow, presumed to be due to photochemical oxidation of Hg(0) via $Br^{\cdot}$ radical and calculated assuming a

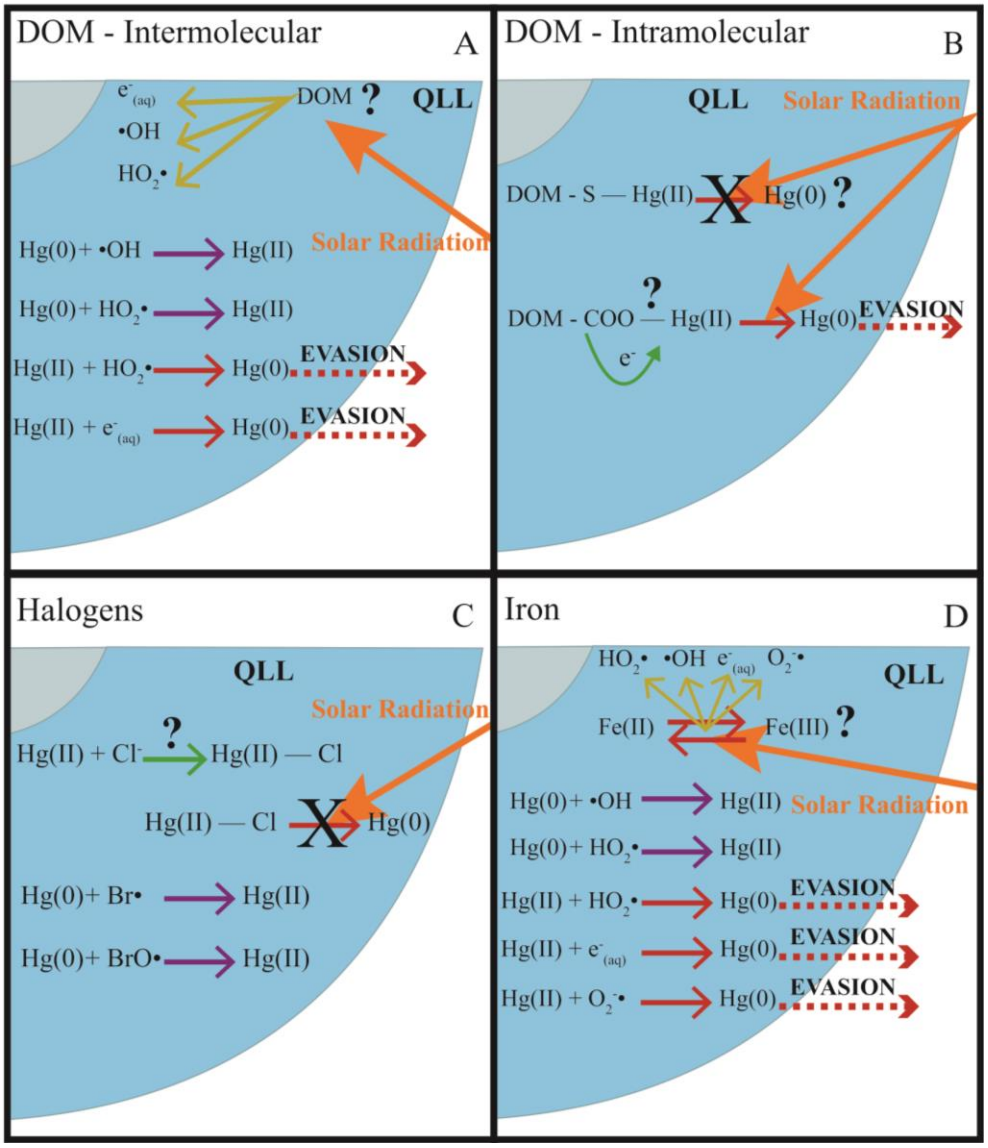

Figure 2.2: Proposed reactions of mercury with DOM (A – intermolecular, B – intramolecular), halogens (C) like chloride and bromine, and iron (D) occurring in the quasi-liquid layer (QLL) of the snow grains. Reactions with significant uncertainty are marked with a question mark, while a large X indicates that this reaction does not go forward when mercury has bound to the specified group. Yellow arrows show processes resulting in the formation of radicals, orange arrows show processes dependent on solar radiation, purple arrows show photooxidation of Hg(0), leading to less Hg(0) emission from the snow, while pink arrows show photoreduction of Hg(II), which leads to the formation of Hg(0) which can be evaded from the snowpack through ventilation or diffusion processes. Green arrows show processes related to the formation of Hg-complexes, either a DOM-charge transfer complex leading to photoreduction of Hg(II) (B), or a Hg-chlorocomplex which is stable and less likely to be photoreduced (C). It should be noted that it is not known whether these reactions occur in the gas phase or the aqueous phase in a snowpack, however, Hg reactions with DOM and iron (A, B, D) have been studied in the aqueous phase, while Hg reactions with Br· and BrO· (C) have been studied in the gas phase and Hg reactions with Cl^- are assumed to occur in the aqueous phase.

second order reaction between Hg(0) and $Br^{\cdot}$, using measured Hg(0) concentrations in snow, as 0.5 - 0.7 $pmol \cdot L^{-1} \cdot hr^{-1}$. However, no rate constants for Hg(0) oxidation in snow have been reported to our knowledge, making a kinetics-based prediction of the rate of Hg(0) oxidation in a snowpack of unknown Hg concentration impossible to determine.

Photodemethylation of MeHg (Fig. 2.1) can result in the loss of MeHg from environmental media (Hammerschmidt and Fitzgerald, 2006; Seller et al., 1996; Suda et al., 1993), while abiotic photoproduction of MeHg has also been observed in temperate lake water (Siciliano et al., 2005). However, though increases in snowpack MeHg with time have been observed, suggesting *in situ* formation of MeHg (Constant et al., 2007), the reactions involved have not been identified, so it is not known if these are photochemical.

2.2.1 Physical variables influencing mercury redox reactions in snow

As a transient, frozen, multi-phase environmental medium, snow is particularly susceptible to variation in environmental conditions which can influence the rate of photochemical reactions within this medium. These variations have the potential to not only modify snowpack chemical and/or physical characteristics, but also to influence the chemical reactions occurring within it. The primary physical environmental factors that have been studied in relation to Hg photochemistry in snow are temperature, irradiation conditions and forest canopy cover.

2.2.1.1 Temperature

Temperature has the potential to modify snowpack reactions in a number of ways, most obviously by changing the physical state of the snowpack or the ratio of solid to liquid water in the snow, and increasing the thickness of the QLL. The rate of Hg photochemical reactions will likely be different in liquid water compared to solid snow (O'Concubhair et al., 2012; Schroeder et al., 2003), with freezing increasing the rate of many reactions (O'Concubhair et al., 2012), including Hg photoreactions (Goodsite et al., 2004). Temperatures below -15 °C are required to photooxidize Hg(0) to Hg(II) in Arctic snow (Brooks et al., 2011), while the presence of liquid water in a frozen temperate or Arctic snowpack can enhance the reduction of Hg(II) to Hg(0) (Kirk et al., 2006; Lalonde et al., 2003). Overall, this may mean that with increases in temperature, Hg(0) photooxidation in the snowpack may be less likely to occur if the snow temperature increases above that -15°C threshold, while Hg(II) photoreduction increases due to greater liquid water content in snowpacks, leading to a greater re-emission of Hg(0) from snow.

A study by Steffen et al. (2002) found that Hg(0) released from Arctic snowpacks appeared to be related to snowpack temperature, with more Hg(0) leaving the snowpack when the snow was warmer; however, this phenomenon was not uniformly observed over their sampling period. Steffen et al. (2002) suggested that an increase in snow temperature may simply serve to facilitate faster evasion of Hg(0) from the snowpack after solar radiation induces reduction of Hg(II) to Hg(0). Steffen et al. (2014) also determined that more atmospheric Hg tends to occur as PHg rather than RGM when temperatures are colder, which would mean deposition of less reactive Hg at colder

temperatures. In a modelling study, Dastoor et al. (2008) also predicted that volatilisation of Hg(0) from the snowpack was related to surface temperatures, with higher temperatures leading to greater volatilisation of Hg(0). In the presence of radiation, temperature may play a key role in the photochemical reduction of Hg(II) to Hg(0), though it is not implicated in directly controlling Hg(0) photoproduction (Ferrari et al., 2005). Bartels-Rausch et al. (2011) determined that decreasing the experimental temperature slowed down photoreduction of Hg(II) in thin ice films. It should be noted, however, that in the absence of radiation, temperature has no measurable effect on Hg(II) reduction in Arctic snow (Dommergue et al., 2007; Durnford and Dastoor, 2011). In a laboratory study of Hg(0) flux from snow, Dommergue et al. (2007) found no significant Hg(0) fluxes to or from temperate, alpine or polar snow when temperatures were increased in the dark, implying that without irradiation, there is no Hg(II) reduction, and neither increases nor decreases in temperature alone will induce oxidation or reduction of Hg in snow (Dommergue et al., 2007; Durnford and Dastoor, 2011).

2.2.1.2 Irradiation

Elemental Hg production in Arctic snow is related to solar irradiation (Ferrari et al., 2005; Poulain et al., 2004), and diurnal cycles in Hg(0) concentrations have been observed in and above the surface of Arctic snow, with maximum Hg(0) concentrations the result of higher intensities of solar radiation (Ferrari et al., 2008, 2005; Steffen et al., 2002). In fact, the most important factor controlling the rate and extent of photochemical reactions of Hg in snow is thought to be irradiation (Durnford and Dastoor, 2011). The

depth to which radiation penetrates in the snowpack will determine the depth to which photochemical reactions can occur in the snow. Many authors have determined different radiation penetration depths, ranging from as little as 3 cm (Brooks et al., 2008a; Poulain et al., 2004) to as much as 60 cm (Dommergue et al., 2003; Faïn et al., 2008a), with roughly 85% of photochemical reactions typically occurring in the top 10 cm of the snowpack (King and Simpson, 2001). The e-folding depth, or depth at which incident radiation is 1/e (~37%) of the intensity at the top surface of the snow, changes depending on the chemical and physical properties of the snowpack, as well as the wavelength range under study (King and Simpson, 2001). Chemical components in the snow causes radiation attenuation; that is, chemicals present will absorb incident radiation to undergo photochemical reactions (King and Simpson, 2001), removing these wavelengths. Physical properties, like snow grain size, snowpack density and the liquid water content of a snowpack influence the depth to which radiation can penetrate in a snowpack by affecting the extent to which radiation is scattered in the snowpack (King and Simpson, 2001), with wetter snowpacks having greater UV penetration (Fisher et al., 2005). Different wavelengths will also penetrate to different depths, with shorter wavelengths having lower penetration depths due to greater scattering (King and Simpson, 2001).

In addition to influencing the radiation penetration depth, the wavelength influences the rate or extent of photochemical reactions of Hg. The ultraviolet (UV) wavelength range 305 – 320 nm is the most important for inducing photochemical reduction of Hg(II) in snow (Dommergue et al., 2007; Lalonde et al., 2003), with UVB radiation (280 – 320nm) generating the greatest Hg(0) evasion from the snowpack

(Poulain et al., 2004). However, in a laboratory experiment examining Hg(II) reduction in thin ice films in the presence of organic matter, Bartels-Rausch et al. (2011) also found that UVA radiation could induce Hg(II) reduction. Hg photooxidation has been observed in some Arctic snowpacks, with oxidation (Hg(0) to Hg(II)) being most efficient under UVA (320 – 400 nm) radiation (Poulain et al., 2004). Photochemical degradation of methylmercury (MeHg) in water is supported by both UV and visible radiation (Chen et al., 2003; Gardfeldt et al., 2001), but UVB typically supports more efficient MeHg photodegradation (Lehnherr and St. Louis, 2009).

2.2.1.3 Forest canopy effects

The presence or absence of a forest canopy influences the extent of Hg(II) reduction in snow. Poulain et al. (2007b) found that less Hg(II) was reduced to Hg(0) in snow under coniferous trees than under leafless deciduous trees, and Hg concentrations in snow under both types of canopy cover were higher than in temperate snow on an ice-covered lake (Poulain et al., 2007b). This difference resulted either from differences in the radiation intensity reaching the surface under the different types of cover (coniferous, leafless deciduous or no cover), or differences in the chemical composition of the snowpack due to vegetation differences (Poulain et al., 2007b). With the presence of canopy cover shadowing the snowpack, less radiation would reach the snow surface, which would result in less Hg(II) photoreduction, and so a greater concentration of Hg(II) remaining in the snowpack. Alternatively, it is possible that the presence of the canopy and vegetation modifies the chemical composition of the snowpack, increasing the

organic matter content, which could influence the rate of Hg reduction in this snow (Poulain et al., 2007b). It was also found that more Hg(II) in snow under temperate forest canopy was associated with particulate matter than in snow under open sky (Poulain et al., 2007b), which may result in the Hg(II) present being less available to undergo photoreduction. In addition, throughfall increases Hg deposition to surfaces underlying the forest canopy (Graydon et al., 2008).

2.2.2 Chemical variables affecting photochemical redox reactions of mercury in snow

The presence of different chemical species will influence the rate and extent of Hg photochemistry in snow. The presence of organic matter, oxidants and ions like chloride or iron can shift the balance of oxidation versus reduction, and can also influence the phase distribution of Hg in the snow, making it more or less available for reaction (Lalonde et al., 2003, 2002).

2.2.2.1 Dissolved organic matter (DOM)

Dissolved organic matter (DOM) is thought to be a collection of organic molecules originating from decomposing organisms, and containing numerous functional groups which may be important for Hg binding and reactions (reviewed by Ravichandran (2004)). Dissolved organic matter plays a somewhat contentious role in Hg photochemical reactions; in water, DOM may either promote/enhance (O'Driscoll et al., 2004; Xia et al., 1999; Zhang, 2006) or inhibit Hg photoreaction (Allard and Arsenie,

1991; Barkay et al., 1997; Garcia et al., 2005), and only a few studies have investigated the link between DOM and Hg photoreactivity in snow (Bartels-Rausch et al., 2011; Kos et al., 2014). The role of DOM may not be as simple as enhancing or inhibiting photochemical reduction of Hg(II), since the presence of other snowpack chemical species may influence how DOM interacts with Hg, and in turn how Hg interacts with incident radiation. DOM may act as an electron donor (Fig. 2.2a, b) in environmental media, by forming a charge transfer complex with Hg, or by generating radicals in the presence of solar radiation (Billing, 1997; Ravichandran, 2004), thereby initiating photochemical reduction of Hg(II) to Hg(0) (Allard and Arsenie, 1991; Bartels-Rausch et al., 2011; Costa and Liss, 1999; Tseng et al., 2004; Xiao et al., 1995; Zhang, 2006). Alternatively, DOM may act to bind and sequester Hg(II) (Fig. 2.2b) through formation of strong bonds with reduced sulfur groups contained in DOM (Xia et al., 1999), making Hg unavailable for photochemical reduction (Amyot et al., 1997). The effects of DOM on MeHg photochemical reactions in snow appear to be unknown. In thin ice films, benzophenone and oxalic acid, two DOM surrogates, may enhance Hg photoreaction; however, temperature and halide concentrations in the ice film will influence the extent of enhancement of Hg photoreactions by organic compounds (Bartels-Rausch et al., 2011). Although little information is available on the action of DOM in Hg reactivity in snow, DOM in natural surface waters has been found to facilitate the photoreduction of Hg(II) to Hg(0) (Poulain et al., 2004). In the presence of sunlight, DOM can form photoreactive intermediates (Blough and Zepp, 1995; Cooper et al., 1988) that can react with Hg, thereby changing the Hg speciation (Bertilsson and Tranvik, 2000). In the absence of studies directly reporting the influence of DOM on Hg reactions in snow,

studies in water can serve as a first step in generating ideas and hypotheses to move the science forward. Early work investigated snow photochemistry by first examining fresh water reactions, and some of the first pictures of snowpack Hg reactivity were derived from such fundamental work (e.g. (Amyot et al., 1994; Zhang and Lindberg, 2001)). As such, while we know now that the rates of Hg photoreaction in snow and liquid water are different (O'Concubhair et al., 2012; Schroeder et al., 2003), such liquid phase work is still valuable in the study of Hg photoreactions in snow.

Concentrations of DOM in remote polar snow are between 0.2 mg/L and 0.7 mg/L (Grannas et al., 2004), an order of magnitude lower than typical values for temperate lakes with moderate DOM concentrations (Xenopoulos et al., 2003), which may have implications for Hg binding to and/or reaction with DOM in snow. In natural waters, strong binding of Hg(II) to reduced sulfur groups may occur (Xia et al., 1999), while weaker binding may occur between Hg(II) and carboxylic acid groups (Fig. 2.2b; (O'Driscoll et al., 2006a; O'Driscoll et al., 2006b)). It may be that the strong binding of Hg(II) to reduced sulfur groups takes some time (days to weeks), while weak binding is faster (Hintelmann et al., 2002). Moreover, the Hg(II) weakly bound to DOM in natural waters may be the photoreducible Hg(II) (O'Driscoll et al., 2006a; O'Driscoll et al., 2006b). This would cause newly deposited Hg(II), which could bind quickly but weakly to carboxylic acid groups, to be photoreducible in a short time frame. Conversely, Hg(II) pre-existing in the water column for some time would have the potential to become strongly bound to reduced sulfur groups, and therefore less photoreducible. The low concentrations of DOM in snow may, therefore, imply that less binding of Hg(II) to

reduced groups will occur, since fewer of these groups are available, and Hg(II) will bind preferentially with reduced sulfur groups if possible (Ravichandran, 2004; Xia et al., 1999), which would mean more phororeducible Hg (Fig. 2.2b). However, it is also possible that with the extremely low concentrations of DOM that exist in snow, little of the snowpack Hg(II) is photoreducible, if DOM is a requirement for Hg(II) photoreduction (e.g. radical production; Fig. 2.2a). The role of DOM in snowpack Hg(II) photoreduction is clearly an area requiring more study.

Another important consideration for the influence of DOM on snowpack Hg photochemistry is pH. The pH of freshly fallen Arctic snow ranges from 4.6 to 6.1 (Camp, 1976; de Caritat et al., 2005). Under these acidic conditions, the binding of Hg to DOM may be influenced as follows: Hg binds to acidic functional groups in DOM such as reduced sulfur and carboxylic acid groups (Ahn et al., 2010) , but under acidic conditions, more of these groups are protonated and unavailable for Hg binding. This decrease in binding would mean that Hg photoreactions are either less or more efficient depending on whether Hg binding to DOM facilitates or inhibits Hg photoreaction, respectively.

2.2.2.2 Snowpack oxidants

Elemental mercury (Hg(0)) present in the snowpack may undergo oxidation to Hg(II), which is then retained and subject to further reactions (Durnford and Dastoor, 2011), although the mechanism of this oxidation, whether photochemical (Lalonde et al., 2003) or occurring in the dark (Faïn et al., 2008a; Ferrari et al., 2004b; Maron et al.,

2008) still represents a great gap in knowledge of snow Hg reactivity. Snowpack oxidants are a diverse group of chemicals that can oxidize other snowpack chemical species, like Hg(0). The exact mechanism of Hg(0) oxidation in snow is not known, but oxidizing agents such as halogen (bromide and bromine oxide) radicals and hydrogen peroxide or hydroperoxy radicals have been identified in the literature (Ferrari et al., 2004a; Lahoutifard et al., 2006).

2.2.2.2.1 Hydrogen peroxide and the hydroperoxy radical

When considering the effect of hydrogen peroxide (H_2O_2) on Hg reduction, it is important to consider the pH of the environment under question. Hydrogen peroxide acts as an oxidant under acidic conditions (Hg(0) to Hg(II)), but a reductant under basic conditions (Hg(II) to Hg(0)) (Fig.2.2a, 2.2d; (Amyot et al., 1994)). The typical pH of rural or remote snow is acidic, ranging from 4.6 – 6.1 (Camp, 1976; de Caritat et al., 2005), which means that H_2O_2 should act as an oxidant. To test this, Lahoutifard et al. (2006) dosed fresh snow samples in Teflon bottles with H_2O_2 then exposed spiked and non-spiked snow samples to ambient solar radiation. Following irradiation, the samples spiked with H_2O_2 had higher concentrations of total Hg, suggesting that the hydroperoxy radical ($HO_2^{\cdot}$) causes an increase in gas phase oxidation of Hg(0) to Hg(II) in the air, allowing the H_2O_2-spiked snow to scavenge atmospheric Hg through the opening of the Teflon bottle (Lahoutifard et al., 2006). Direct oxidation of Hg(0) by the $HO_2^{\cdot}$ radical is, however, neither a fast nor effective process (Kobayashi, 1987; Tokos et al., 1998), which may indicate that some indirect oxidation occurs in snow involving the $HO_2^{\cdot}$

radical and Hg (Lahoutifard et al., 2006). Lin and Pehkonen (1999) also proposed the $HO_2^{\cdot}$ radical as a snowpack oxidant of Hg(II); however, Gardfeldt and Jonsson (2003) determined that reduction by the $HO_2^{\cdot}$ radical in water is not the major pathway for Hg(II) reduction, and Ferrari et al. (2004b) determined that daytime production of $HO_2^{\cdot}$ radical in a snowpack at Station Nord, Greenland was limited. Oxidation of Hg(II) in Arctic snow has been observed at night at Station Nord in Greenland (Ferrari et al., 2004b), which would require the presence of night time snowpack oxidants. In rural temperate locations $HO_2^{\cdot}$ formation has in fact been observed at night (Holland et al., 2003), but this has not been observed in Arctic locations, which may mean that other oxidants need be considered to explain Hg(0) oxidation in Arctic snow (Ferrari et al., 2004b).

2.2.2.2.2 Halogens and halogen radicals

Atmospheric oxidation of Hg, particularly during atmospheric mercury depletion events (AMDEs) occurring in the spring in the Arctic, appears to occur via reaction with halogen or halogen oxide radicals ($Cl^{\cdot}$, $ClO^{\cdot}$, $Br^{\cdot}$ or $BrO^{\cdot}$) (Ariya et al., 2009; Lin and Pehkonen, 1998; Wang and Pehkonen, 2004) or via ozone or hydroxyl radical reaction at inland sites (Lin and Pehkonen, 1999; Munthe, 1992). It is not known whether these same species are responsible for snowpack Hg oxidation, though oxidation by O_3 is probably too slow to be important, as determined by recent modelling work (Holmes et al., 2010, 2006). Bromine ($Br^{\cdot}$) and bromine oxide ($BrO^{\cdot}$) radicals are the most efficient oxidizers

of Hg(0) in the gas phase (Ariya et al., 2002; Holmes et al., 2009), and are proposed to be the major oxidants transforming Hg(0) to Hg(II) during AMDEs. The reaction of Hg(0) with the bromine radical is a fast process (Ariya et al., 2002), and at colder temperatures the gas phase oxidation of Hg(0) by the bromine radical is predicted to be faster (Goodsite et al., 2004). Note, however, that this is a predicted result from theoretical calculations as Hg(0) oxidation by bromine has only been studied at room temperature (Stern et al., 2012). The production of the bromine radical from molecular bromine requires much less energy than the production of the $HO_2^{\cdot}$ radical, making this a more likely gas phase Hg(0) oxidation pathway in snow (Ferrari et al., 2004b). Ferrari et al. (2004b) concluded that bromine and bromine oxide radicals are the primary gas phase oxidants of Hg(0) in the daytime Arctic snowpack (Fig. 2.2c), and Brooks et al. (2006) found Hg and bromine chemistry to be linked, where the reaction of bromine and Hg leads to the formation of reactive gaseous mercury (RGM) from Hg(0) in the gas phase. In particular, the bromine oxide radical of marine origin increases in concentration when ozone is present, in what is known as a "bromine explosion" (Barrie and Platt, 1997; Frieß et al., 2004; Wennberg, 1999), and Hg(0) is removed from the air as Hg(II). Similar patterns in bromine oxide radicals and Hg(0) in air have also been observed (Sommar et al., 2004), with maxima at midday and minima at night. These increases in air Hg(0) may be linked to the production and evasion of reduced Hg(0) from snow (Ferrari et al., 2008; Steffen et al., 2005).

Chloride (Cl^-) is another halogen ion that can play an important role in Hg photoreactions in snowpacks (Fig. 2.2c). Greater reduction of Hg(II) to Hg(0) has been

observed in snow with lower concentrations of Cl^-, and the addition of Cl^- to melted snow prior to exposure to UVB radiation results in a decrease in aqueous phase Hg(II) reduction (Lalonde et al., 2003). In fresh snow, the addition of Cl^- limits the loss of Hg(II) from the snow by decreasing Hg reduction (Lalonde et al., 2003). Some researchers suggest that Hg(II) chlorocomplexes are relatively stable and unlikely to undergo photoreduction, and with higher Cl^-, more chlorocomplexes form (Fig. 2.2c; (St. Louis et al., 2007)). Qureshi et al. (2010), for example, identified a chlorocomplex as a product of Hg photooxidation in sea water, and this product was not easily reducible. It has further been determined that Hg(0) photooxidation in snow is favoured over photoreduction in the presence of Cl^- ion (Amyot et al., 2003).

Snow near open water leads in Arctic sea ice has a much higher concentration of Hg(II) than overland snow (Brooks et al., 2008b; Douglas et al., 2005; St. Louis et al., 2007), and frost flowers, which form near sea ice leads and polynyas and have high halogen concentrations, may scavenge Hg(II) from the atmosphere (Douglas et al., 2005; Sherman et al., 2012) due to the high Cl^- content. As the Cl^- concentration increases in snow, Hg(II) tends to exist as less reducible chlorocomplexes and so remains in the oxidized state (St. Louis et al., 2007). A positive correlation between the Cl^- and total Hg content of snow has also been observed, implying that Cl^- preserves Hg(II) in snow (Garbarino et al., 2002; Larose et al., 2010; Poulain et al., 2007a, 2004; Steffen et al., 2013; St. Louis et al., 2007). Snow from the Experimental Lakes Area in Ontario, Canada, incubated under solar radiation on site, also showed greater photoreduction of Hg(II) to Hg(0) when Cl^- concentrations in snow were lower (Lalonde et al., 2003).

In snow over sea ice with higher Cl^- concentrations, Poulain et al. (2007a) found more Hg(II) was bound to particulate matter than in low Cl^- snow. In contrast, in a controlled laboratory study, Mann et al. (2011) found that acidic, laboratory-synthesized snow with added Cl^- showed more Hg(II) free in melted snow fractions, while Hg in synthesized snow containing no salt at a neutral pH had a higher fraction bound to particulate matter. In soils with pH < 7, the presence of chloride results in less binding of Hg to particles, while in neutral or basic environments, Hg binding to particles is not influenced by the presence of Cl^- (Barrow and Cox, 1992; Lumsdon et al., 1995; Novotny et al., 1998; Yin et al., 1996). Road salt applied to snowpacks can cause the release of heavy metals bound to organic matter in the soil under the snowpack due to the presence of high Cl^- concentrations (Backstrom et al., 2004). This could mean that Cl^- does not simply influence the rate of Hg photoreduction by forming less reducible chlorocomplexes, but also influences Hg binding to particulate matter, given the correct pH conditions, which in turn may also influence Hg photoreactivity.

2.2.2.3 Iron

Iron (Fe) is known to influence Hg photochemical reactions in natural water systems; however, the influence of Fe on snowpack Hg photochemistry has not been explicitly studied. Iron exists as ferrous (Fe(II)) and ferric (Fe(III)) ions in natural waters and Fe(II) addition may enhance Hg(II) photoreduction in natural waters by up to 470% when dissolved organic matter is also present (Zhang and Lindberg, 2001). Photochemical cycling of Fe between the ferrous and ferric ions (Fig. 2.2d) results in the

production of radicals such as $HO_2^{\cdot}$ and $^{\cdot}OH$ that can induce oxidation and/or reduction of Hg in natural waters (Amyot et al., 1994; Hammerschmidt and Fitzgerald, 2010; Zhang and Lindberg, 2001). Since Fe is present in atmospheric snow (Zhuang et al., 1995), it will be deposited to the surface where it may undergo reactions to produce radicals and induce Hg reactions in snow (Fig. 2.2d). In atmospheric snow, 25 – 74% of the total filterable Fe may be present as Fe(II), and in rain water Fe may be 25 – 53% Fe(II) (Zhuang et al., 1995), or up to 70 % Fe(II) (Kieber et al., 2003). Since the action of Fe on Hg reactions depends on Fe speciation, these similarities in rain and snow Fe speciation may result in similarities in Fe reaction rates and extents in snow and natural water environments. It is likely, however, that the rate and/or extent of Fe reactions in snow will differ somewhat from those seen in natural waters, since the rates of reactions in frozen and liquid aqueous media are different (O'Concubhair et al., 2012).

2.2.3 Speciation effects on mercury photooxidation and photoreduction reactions in snow

The above sections deal primarily with reactions involved in the cycling between reduced Hg (Hg(0)) and oxidized Hg (Hg(II)); however the influence of partitioning of Hg between free and particle bound phases, or how MeHg may react in snowpacks must also be considered, as these factors are involved with Hg photochemical reactions in snow. Speciation or phase association is an important criterion when considering Hg behaviour since the presence of "free" or reactive Hg versus Hg bound to particulate matter will influence how that Hg reacts, or whether it is able to undergo photochemical

reactions at all. Methylmercury (MeHg, $CH_3Hg(I)$), a toxic and bioaccumulative organic ion of Hg (Fitzgerald and Clarkson, 1991), is present in frozen and melted snow but is not simply a Hg reaction endpoint, with bioaccumulation a foregone conclusion. Rather, MeHg is a photoreactive species itself, and also has the ability to be bound by particulates and organic matter, which will affect MeHg bioavailability (Hammerschmidt and Fitzgerald, 2006; Sellers et al., 2001; Skyllberg, 2008; Skyllberg et al., 2006; Wängberg et al., 2006).

Reactive vs. particle bound mercury

Most of the total Hg present in a typical polar, alpine or temperate snowpack is particle bound, with only a small fraction of unbound Hg(II) (Balogh et al., 2000; Dommergue et al., 2007; Faïn et al., 2008a; Poulain et al., 2007b; St. Louis et al., 2007). Hg can be particle bound when it is deposited to the snowpack (PHg) due to dry deposition or particle scavenging processes by snow (Ariya and Ryzhkov, 2003; Poissant et al., 2008; Prestbo and Gay, 2009; Zhang et al., 2009); in addition, Hg can move between particle bound and unbound forms in the snowpack over time (Durnford and Dastoor, 2011). However, the extent of binding of Hg(II) to particulate matter (PM) in frozen or melting snow will be dependent upon chemical conditions. Binding of Hg to PM may make it unavailable for chemical or biological reactions; consequently, knowing the fraction of Hg that is free is imperative for accurate prediction of the environmental implications of snowpack Hg (Larose et al., 2010; Witherow and Lyons, 2008).

When more Hg(II) in a snowpack is present as “free” Hg(II), as opposed to particle bound Hg (PHg), as much as half of the deposited Hg(II) can be photoreduced

and lost from the snowpack within 24 h (Durnford et al., 2012; Lalonde et al., 2003, 2002). Hg deposited by AMDEs in the spring in Arctic and sub-Arctic regions tends to be primarily free Hg(II) as opposed to PHg (Brooks et al., 2006; Sherman et al., 2012), although greater proportions of PHg have also been proposed depending on atmospheric conditions when the AMDE occurs (Larose et al., 2011; Steffen et al., 2014, 2013). This may account for the >50% loss of AMDE-deposited Hg that is seen within 24 h following the depletion event (Lalonde et al., 2002), with such Arctic surface snow losing up to 90% of AMDE deposited Hg within 48 h (Poulain et al., 2004). In contrast, in snow above high elevation glaciers in Tibet, less than a third of the deposited Hg was reduced to Hg(0) and lost over the entire frozen snow period (Huang et al., 2012). Huang et al. (2012) found that Hg in this high elevation glacial snow was present primarily as PHg, and attributed the lack of Hg photoreduction to this lack of free Hg(II). In a temperate snowpack, Balogh et al. (2000) found that approximately 90% of the Hg present was PHg, while Poulain et al. (2007b) determined that 70 – 80% of the Hg present in temperate snow under varying canopy covers was bound to particles. These studies indicate that temperate snow may have a relatively low fraction of photoreducible "free" Hg(II) present as compared to Arctic snow, particularly during the AMDE season, but this would depend on the ratio of bound to unbound Hg(II) present in snow. An additional complication is the conversion between particle bound and free Hg(II), which will occur over the lifetime of the snowpack (Durnford and Dastoor, 2011). This conversion means there is the possibility of the unavailable PHg becoming available for photoreduction or methylation in the snowpack, or conversely, free Hg(II) becoming

unavailable for photoreduction after binding to snowpack particles (Durnford and Dastoor, 2011).

Methylmercury photoreactivity

Methylmercury (MeHg) is the Hg species of greatest environmental health concern, due to its toxicity and ability to bioaccumulate (Chang and Hartmann, 1972; Hammerschmidt et al., 2002). In particular, bioavailable MeHg, or that MeHg that can be taken up by organisms at the base of the foodchain, entering and existing in aquatic ecosystems is cause for concern. Methylmercury can form and degrade in various environmental media. Abiotic photoproduction of MeHg has been observed in the upper sunlit portions of some temperate lakes, in the presence of DOM (Siciliano et al., 2005). Degradation of MeHg occurs through microbial action (Compeau and Bartha, 1984; Oremland et al., 1991), but can also occur through photochemical reaction (Constant et al., 2007), which is induced primarily by UV radiation (Lalonde et al., 2001; Wängberg et al., 2006). Recent work by Lehnherr et al. (2012) named photochemical demethylation of MeHg as the primary sink of MeHg in Arctic wetlands. Methylmercury has been detected in snow (Constant et al., 2007; Dommergue et al., 2010; Lahoutifard et al., 2005), and up to 7.6% of the total Hg in an Arctic snowpack may be MeHg, based on one study area in the low Arctic tundra (Constant et al., 2007). It is further known that snowmelt water is a significant source of MeHg to Arctic water bodies (Loseto et al., 2004a) but little knowledge of the activity of MeHg in snow exists. It has been concluded by some that MeHg forms in the snow itself (Constant et al., 2007), although this snowpack formation of MeHg is not uniformly accepted (Lahoutifard et al., 2005). Dommergue et al. (2010)

found increasing MeHg concentrations in Arctic snow from low levels in mid-April to higher concentrations in early June, prior to snowmelt. It was not clear whether these increases in MeHg were due to deposition of MeHg from the atmosphere, or formation in the snowpack, either by biotic or abiotic photochemical methylation processes (Dommergue et al., 2010). Bacterial activity has been observed in Arctic snow (Carpenter et al., 2000; Felip et al., 1995; Junge et al., 2004; Priscu et al., 1998), and it has been proposed that snowpack microorganisms may interact with snowpack Hg(II) to form MeHg (Amato et al., 2007). However, Constant et al. (2007) found no correlation between sulfate-reducing bacteria numbers and MeHg concentrations in snow, suggesting that anaerobic organisms may not be responsible for biotic methylation of Hg in snow. For further information on the activity of microorganisms in snow and the formation of MeHg, please see work by Barkay and Poulain (2007), as well as Larose et al. (2013a) for detailed work in Arctic snow, and work by Lehnherr and St. Louis (2009) for detailed study of photodemethylation in Arctic freshwater lakes.

Studies investigating the photoreactivity of MeHg in snow are lacking, although it has been postulated that abiotic reactions may lead to production or destruction of MeHg in snow (Constant et al., 2007). Since snow is an oxygenated medium, it is likely that reactions requiring anoxic conditions for methylation/demethylation, such as those occurring in sediments by sulfate-reducing bacteria (Gilmour and Henry, 1991), will not occur to an appreciable degree in snow. However, Larose et al. (2013b) did suggest microbial production of MeHg in snow. There have, however, been studies regarding Hg methylation/demethylation in natural waters, in particular with an emphasis on surface

waters, and these may provide a starting point for looking at the activity of MeHg in snow. Photodegradation has been identified as the most important MeHg degradation process in natural freshwater and surface ocean systems over microbial demethylation, which is much slower in these media (Hammerschmidt et al., 2006; Hammerschmidt and Fitzgerald, 2006; Krabbenhoft et al., 2002; Lehnherr et al., 2012; Lehnherr and St. Louis, 2009; Seller et al., 1996; Sellers et al., 2001). In natural waters, MeHg photochemical degradation occurs in the presence of both visible and ultraviolent (UV) radiation (Chen et al., 2003; Gardfeldt et al., 2001; Siciliano et al., 2005), with UV radiation-induced degradation being more efficient (Lehnherr and St. Louis, 2009). Further, radiation intensity is important, with higher intensities leading to faster photodemethylation (Bonzongo and Donkor, 2003). Radiation can penetrate up to 60 cm Arctic snow (Dommergue et al., 2003; Faïn et al., 2008b), with 85% of reactions occurring in the top 10 cm (King and Simpson, 2001), making MeHg photoreactions, possible in this region, if they occur. The rate of photodemethylation of MeHg is unaffected by differences in the pH and presence of particulates in freshwater systems (Hammerschmidt and Fitzgerald, 2006; Lehnherr and St. Louis, 2009; Seller et al., 1996; Sellers et al., 2001). The presence of chloride in sea water, however, does affect the photodemethylation rate through the formation of less reactive chloro-complexes with Hg (Lehnherr et al., 2011; Morel et al., 1998). Such chlorocomplexes are also thought to occur in Arctic snowpacks (St. Louis et al., 2007), which could then influence photodemethylation of MeHg, with less demethylation occurring in Arctic snow near leads and polynyas where chloride concentrations are higher (Sherman et al., 2012). While photodegradation of MeHg may be a major MeHg degradation process in fresh waters, a study by Siciliano et al. (2005)

found that photochemically-induced formation of MeHg was possible in some freshwater systems, though not uniformly observed in their study, and found to be dependent on the chemical composition of the lake under investigation. This could mean that the abiotic methylation of Hg postulated by Constant et al. (2007) to occur in Arctic snow may be photochemical in nature. Taken together, these studies may indicate that abiotic Hg methylation and demethylation are possible in the upper sunlit portions of a snowpack, if solar radiation and DOM are present, and if observations in natural waters hold true in sub-zero environments.

2.3 Arctic Implications

In the Arctic, higher trophic level marine mammals and humans have been observed to have far greater Hg concentrations than their typical temperate counterparts (AMAP, 2011; Braune et al., 2005; El-Hayek, 2007). For example, Inuit mothers have been found to have up to an order of magnitude more Hg than the average US woman, based on measurements in hair (Muckle et al., 2001). Some ecosystems, may be more efficient at accumulating Hg, despite not necessarily having greater inputs (Evers et al., 2007). Such ecosystems have been described as "mercury sensitive", meaning that the same amount of Hg(II) coming in results in higher concentrations in organisms than may be seen elsewhere (Evers et al., 2007). This sensitivity could result from a number of factors including: a greater rate of formation of MeHg and/or slower rate of destruction of MeHg; greater retention of Hg(II) and/or more efficient methylation, or food web structures that result in greater bioaccumulation (Clayden et al., 2013; Evers et al., 2007).

Experimental evidence has shown that an increase in Hg loading in lakes results in a proportional increase in the MeHg loading in lake biota (Orihel et al., 2007). However it should be noted that not all Hg present in an ecosystem will be bioavailable (Larose et al., 2011, 2010), and so not all Hg(II) will be methylated, although Hg deposited to the Arctic AMDEs during polar spring is readily bioavailable (Larose et al., 2011; Lindberg et al., 2002; Scott, 2001). Hg(II) can undergo chemical and photochemical reactions resulting in stable or volatile inorganic forms, and therefore less MeHg bioaccumulation in organisms. It is thus important to quantify Hg dynamics in Hg-sensitive regions, like the Arctic and understand the ways in which various environmental media can contribute to Hg accumulation.

Since Arctic pollution with Hg is dependent on long range transport processes, monitoring and control of Hg emissions is a global effort. In January of 2013, an international legally binding agreement, the Minimata Convention on Hg, was finalized by the United Nations Environment Program (UNEP) (Kohler et al., 2013). This convention aims to reduce global Hg emissions by approaching the issue from a global perspective and phasing out many Hg-containing products. With Hg emission thresholds being implemented, existing uncertainty in Hg emissions budgets should be reduced. To date, measurements of Hg wet deposition have been undertaken, with monitoring of Hg concentrations in precipitation being measured by several networks such as the mercury deposition network (MDN), European monitoring and evaluation programme (EMEP) and the global mercury observation system (GMOS), or predicted using atmospheric models (Subir et al., 2012, 2011). However, many of these networks, including the

Mercury Deposition Network (MDN) in North America, ignore the dry deposition of Hg (Herrick, 2009), which occurs when precipitation is not falling (Lindberg et al., 2007). This means that accurate prediction of the total amount of Hg that will deposit to surfaces like snowpacks is challenging, especially because networks like the MDN do not presently make remote northern measurements, and the sampling systems used may not be effective at cold northern temperatures. A network with increased spatial resolution is necessary before accurate prediction of Hg deposition is possible for specific ecosystems (Ryaboshapko et al., 2007), and without accurate predictions of Hg deposition to the surface and the present lack in understanding of snowpack Hg cycling behaviour (Durnford et al., 2012), reliable predictions of Hg movement through the Arctic are difficult to obtain.

3 Conclusions and knowledge gaps in snowpack mercury fate

To quantify the Hg released to surface waters from a melting snowpack, it is necessary to know the volume of snowmelt and the Hg concentration in the snowmelt. The initial concentration in the snowpack will vary through the seasons with changing inputs from deposition and losses through volatilization. Unfortunately, neither global atmospheric Hg emissions nor Hg deposition rates are well constrained (Lin et al., 2005; Seigneur et al., 2004; Walcek et al., 2003), although more recent global emissions estimates are improving (Pirrone et al., 2010). Snow is a complex and dynamic environmental medium in which many photochemical reactions of Hg can occur (see

Figs. 2.1, 2.2). Unfortunately, many of these reactions are poorly studied and uncertain (Fig. 2.2).

One of the greatest gaps in knowledge of Hg fate in snow is in the measurement of photooxidation and photoreduction reactions and identification of the underlying mechanisms. The primary oxidants of Hg(0) as well as the Hg oxidation products are not known. It may be that species like halogen or halogen oxide radicals (Fig. 2.2c) are primarily responsible, but the mechanisms have not been clarified. Photoreduction of Hg is also an area with many uncertainties. The photoreduction of Hg(II) will result in the formation of Hg(0); however, the primary reductant of Hg(II) in snow also has yet to be identified. The hydroperoxy radical (Pehkonen and Lin, 1998) or sulfite (Munthe et al., 1991; VanLoon et al., 2000) are known atmospheric Hg(II) reductants that may be responsible.

Environmental models are useful tools for examining our current understanding of Hg movement through the environment, and for predicting the influences of climate change on Hg cycling (Durnford et al., 2012). Unfortunately, current models are limited by a lack of Hg snowpack reaction data, relying on simplistic reaction mechanisms to describe the complicated cycling (Dastoor et al., 2008), or relying on set Hg(0) reemission percentages due to incomplete understanding of Hg(II) reduction in snow (Holmes et al., 2010). Outridge et al. (2008) developed a mass balance of Hg for the Arctic Ocean and quantified various Hg sources. It was concluded that total atmospheric deposition was the greatest source of Hg to the Arctic Ocean (Outridge et al., 2008); however, variable emission/deposition fluxes for snow increase the uncertainty in these

modeled results. Model work by Fisher et al. (2013) concludes that the interannual variability of total Hg in Arctic Ocean surface water is driven primarily by the movement of Hg from melting snow over sea ice. A recent model by Durnford et al. (2012) was the first to include a dynamic representation of Hg deposition to and reemission from the snowpack, allowing much better prediction of atmospheric and Arctic snowpack Hg concentrations over time. Even with these advances, there is still more work to be done. Identifying the reaction rates arguably may be more important than identifying the specific mechanisms. Knowledge of the overall rates of Hg reactions in snow would allow creation of kinetics-based predictive models even if the specific sub reactions are not known, which would further increase the accuracy of models like the one Durnford et al. (2012) developed. It is further important to determine where these reactions occur, specifically, whether they are gas phase reactions, reactions in the quasi-liquid layer, or heterogeneous reactions at the solid/gas interphase. While some researchers have determined rates of photochemical oxidation or reduction of Hg in snow, the values are only strictly applicable at the time and location of study (Durnford and Dastoor, 2011) due to the wide array of environmental variables. The dependence of rate constants on environmental conditions (temperature, radiation conditions, snowpack chemical conditions) have not yet been sufficiently quantified, and this needs to be done to model Hg cycling in snow to its full complexity.

Another area of recent research with very little data is the input, production and destruction of methylmercury (MeHg) in an Arctic snowpack. MeHg has been measured in Arctic snow, with concentrations from <10 pg/L to >200 pg/L reported (Constant et

al., 2007; Dommergue et al., 2010; Lahoutifard et al., 2005; Lehnherr, 2014); however, it is not known whether this MeHg is derived from atmospheric deposition, or if there is MeHg production within an Arctic snowpack. It is also not yet known if MeHg degradation is photochemical or microbial in a snowpack (Constant et al., 2007). Without knowledge of the formation and destruction of MeHg in snowpack, it is impossible to accurately predict the amount of MeHg that can be expected to enter a receiving water body from snowmelt during the spring.

It is very difficult to predict the effects of changing the chemical nature of a snowpack or how changing environmental conditions will influence the extent and rate of photochemical reactions of Hg in snow. Identification of the specific reactions responsible for photochemical oxidation and reduction of Hg, formation and/or destruction of methylmercury may allow for mechanistic predictive models to be developed and related to variables such as climate. This knowledge would also allow scientists to predict how Hg movement through environmental media may be modified with changing climate conditions in the future, especially in regions like the Arctic where climate conditions are rapidly changing and increases to the volume of snowfall and earlier snowmelt are predicted to occur (ACIA, 2005; AMAP, 2011; IPCC, 2007). The quantification of Hg speciation and fate in a snowpack may allow for the prediction of the changes in Hg retention in snowpacks. Changes in Hg retention and snow melt behaviour will directly influence the exposure of aquatic organisms to Hg. Future research efforts should focus on determining rates of Hg reduction in snow, and how environmental and snowpack chemical properties influence these reactions. The role of chemical species like

halogens and dissolved organic matter in reduction and oxidation mechanisms also need to be defined so that the influence of changes to environmental conditions can be predicted. Filling these research gaps will allow for better quantification of the future risks to ecosystem and human health from Hg contamination particularly in Polar Regions.

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CHAPTER 3: MERCURY IN ARCTIC SNOW: QUANTIFYING THE KINETICS OF PHOTOCHEMICAL OXIDATION AND REDUCTION

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Abstract

Controlled experiments were performed with frozen and melted Arctic snow to quantify relationships between mercury photoreaction kinetics, ultra violet (UV) radiation intensity, and snow ion concentrations. Frozen (-10°C) and melted (4°C) snow samples from three Arctic sites were exposed to UV (280 – 400 nm) radiation (1.26 – 5.78 $W \cdot m^{-2}$), and a parabolic relationship was found between reduction rate constants in frozen and melted snow with increasing UV intensity. Total photoreduced mercury in frozen and melted snow increased linearly with greater UV intensity. Snow with the highest concentrations of chloride and iron had larger photoreduction and photooxidation rate constants, while also having the lowest Hg(0) production. Our results indicate that the amount of mercury photoreduction (loss from snow) is highest at high UV radiation intensities, while the fastest rates of mercury photoreduction occurred at both low and high intensities. This suggests that, assuming all else is equal, earlier Arctic snow melt periods (when UV intensities are less intense) may result in less mercury loss to the atmosphere by photoreduction and flux, since less Hg(0) is photoproduced at lower UV intensities, thereby resulting in potentially greater mercury transport to aquatic systems with snowmelt.

1 Introduction

Mercury (Hg) is a toxic contaminant that moves into aquatic ecosystems in many ways, including snowmelt in the spring, and can bioaccumulate and biomagnify in Arctic food webs (Atwell et al., 1998; Swanson and Kidd, 2010). The environmental behavior of

Hg is dependent on its speciation. Elemental Hg (Hg(0)) has a high vapour pressure and is the primary form of Hg in the atmosphere (Lindqvist and Rodhe, 1985; Morel et al., 1998; Wängberg et al., 2007), in the air spaces of soils and snow (Dommergue, 2003; Fain et al., 2006; Ferrari et al., 2004b; Moore and Castro, 2012; Obrist et al., 2014; Sigler and Lee, 2006), and as dissolved gaseous Hg in water (O'Driscoll et al., 2008). Oxidized forms of Hg (Hg(II), free or within organic complexes) predominate in condensed phases such as natural waters (Morel et al., 1998; Ullrich et al., 2001), sediments (Bloom et al., 1999), the water-filled pores and solid phases of soils (Skyllberg, 2011), and in snow (Ferrari et al., 2004a; Poulain et al., 2007). Methylmercury (MeHg) is the bioaccumulative form of Hg (Atwell et al., 1998; Bartels-Rausch et al., 2011), and the formation of MeHg in ecosystems depends on, among other factors, the presence of Hg(II) (Mason and Sheu, 2002). The Arctic is a region where Hg retention is of significant interest due to high Hg concentrations reported in Arctic biota (Carrie et al., 2010; Kirk et al., 2012; Muir et al., 1992), and a predicted 25% increase in atmospheric inputs by 2020 (AMAP, 2011). This presents potential problems for Arctic indigenous populations who rely heavily on higher trophic level wildlife such as marine mammals as a food source (Barrie et al., 1992; Kinloch et al., 1992). To predict increasing Hg loading to Arctic biota, it is necessary to develop predictive models incorporating reactions regulating Hg retention and movement between Arctic environmental media (snow, air, water).

Snow and snowmelt are important ways for Hg(II) to move within and between Arctic ecosystems. Snow is a complex environmental medium consisting of solid,

gaseous and liquid phases, and it can scavenge Hg and particles from the atmosphere (Ebinghaus et al., 1999; Gardfeldt et al., 2001; Schroeder and Munthe, 1998). Hg can also be deposited to snow via dry gaseous or dry particle deposition (Cobbett et al., 2007; O'Driscoll et al., 2005; Schroeder and Munthe, 1998). Once present in snow, Hg is labile, undergoing reactions and changing speciation (Lalonde et al., 2002; Poissant et al., 2008; Schroeder and Munthe, 1998). In Arctic and sub-arctic regions, atmospheric Hg can be deposited to the snow surface by atmospheric mercury depletion events (AMDEs) (Ariya et al., 2004, 2002; Kirk et al., 2006; Schroeder et al., 1998; Sherman et al., 2010; Steffen et al., 2008), resulting in total Hg (THg) concentrations in snow as high as 820 $ng \cdot L^{-1}$ (Douglas et al., 2005). Some research suggests this is a transient effect, with snow THg concentrations falling to pre-AMDE levels within 24 to 48 hours due to the labile nature of AMDE-deposited Hg, which is quickly reduced and lost from snow (Aspmo et al., 2006; Dommergue et al., 2010; Kirk et al., 2006). Still other research suggests that AMDEs represent a significant source of Hg to Arctic snow since some deposited Hg is retained and transported with snow melt (Dommergue et al., 2003; Hirdman et al., 2009; Johnson et al., 2008; Loseto et al., 2004; Steffen et al., 2005).

The environmental fate of Hg depends on its speciation and this is critical to the discussion concerning deposition and retention processes in Arctic snow. Oxidized Hg, or Hg(II), is the form that remains in the snowpack, and has the ability to be transformed into the bioaccumulative and toxic methyl mercury, while reduced Hg, or Hg(0), is volatile and does not sorb appreciably to ice crystals (Bartels-Rausch et al., 2008; Ferrari et al., 2004a), so it will tend to be removed from a snowpack, with wind pumping

accelerating this removal (Faïn et al., 2013; Ferrari et al., 2005). This means that a greater fraction of Hg(II) and more photooxidation (formation of Hg(II) from Hg(0)) than photoreduction makes a snowpack a greater Hg source to aqueous environments upon melt.

Photochemical reactions have been identified by many researchers as critical mechanisms driving Hg oxidation and reduction in snow (Durnford and Dastoor, 2011; Lalonde et al., 2002; Poulain et al., 2004); however, limited data are available and often assume linear kinetics, that is, linear relationships between radiation and rates (Durnford and Dastoor, 2011). Lalonde et al. (2003) and Poulain et al. (2004) determined that Hg oxidation can occur in snow, but no kinetic rates were derived. Fain et al. (2006) found the rate of Hg(0) oxidation in snow to be 0.5 - 0.7 $pmol \cdot L^{-1} \cdot hr^{-1}$, but did not report a rate constant. Dommergue et al. (2007) measured reduction rate constants of 0.25 h^{-1} or 0.18 h^{-1} by continuously monitoring the decrease in Hg in headspace above irradiated snow over time. Other groups have determined the rate of Hg reduction in snow to range between 0.25 $pmol \cdot L^{-1} \cdot h^{-1}$ and 1.60 $pmol \cdot L^{-1} \cdot h^{-1}$, but no rate constants have been reported, and these determinations were based on a limited number of available data points (Lalonde et al., 2003, 2002; Poulain et al., 2007, 2004). This wide variation in reaction rates, up to a six-fold difference, makes the development of an accurate predictive model difficult (Dastoor et al., 2008; Durnford and Dastoor, 2011; Soerensen et al., 2010), and the assumption of linearity used to determine kinetics, while true over short time periods, may not necessarily hold true over longer time frames (e.g., daily or seasonally), meaning that the predicted rates may not be accurate. With this wide range in

oxidation and reduction rates, it is difficult to say whether oxidation (maintenance or increase of Hg levels in snow) or reduction (potential loss of Hg from snow) in snow is dominant or faster, since reported oxidation rate constants are on the same order as reported reduction rate constants.

The variability in reported reaction rates is likely due to differences in sampling and analytical techniques, combined with an inability to control the wide range of chemical and physical variables affecting *in situ* measurements of Hg speciation and oxidation/reduction (Durnford and Dastoor, 2011; Mann et al., 2014). Sequestration of reactive Hg by dissolved organic carbon (DOC) and chloride ions (Cl^-), or photosensitization of reactions by DOC, may be important in determining the balance of photoreduction and photooxidation in the snowpack. In natural waters, DOC is important to Hg photoreactions (Xiao et al., 1995; Zhang, 2006); it should be noted, however, that very little is known about DOC action in snow, and as such, relationships determined in natural water systems may not hold true in snow. Chloride has been found to enhance Hg photooxidation, or suppress Hg photoreduction in snow (Lalonde et al., 2003), thereby influencing the kinetics of Hg reaction. In addition, physical variables such as the energy and spectra of the incident radiation are also important (Bartels-Rausch et al., 2011; Lalonde et al., 2003; St. Louis et al., 2007). Several researchers have proposed ultraviolet-B (UVB) radiation (280 – 320 nm wavelengths) as a primary driver of Hg reduction in snow (Dommergue et al., 2007; Durnford and Dastoor, 2011; Lalonde et al., 2003). In contrast, Bartels-Rausch et al. (2011) found ultraviolet-A (UVA) radiation (320 - 400 nm) induced Hg reduction in ice film experiments, and Fain et al. (2007)

determined that UVA radiation plays an active role in Hg photochemical processes in snow. While there are few studies examining Hg photooxidation in snow, UVA radiation has been proposed as the driving variable (Durnford and Dastoor, 2011). Although the balance of photoreduction and oxidation processes is still unclear, studies suggest there is predominantly a net reduction effect with exposure to natural solar radiation (Ariya et al., 2004; Lalonde et al., 2003, 2002). However, the effects of UV irradiation intensity on the separate processes of Hg photochemical oxidation and reduction in snow have not been determined.

Currently, there are knowledge gaps surrounding the effects of irradiation intensity, irradiation quality, Cl^-, and DOC on the fundamental processes of Hg photochemical oxidation and reduction in frozen snow (reviewed in Durnford and Dastoor (2011) and Mann et al. (2014)). As such, accurate predictive models are difficult to develop and have limited our ability to predict the distribution of Hg in polar ecosystems affected by a changing climate. In this study, we used controlled experiments to examine the influence of these factors on Hg photoreduction in Arctic snow, and made the following hypotheses: (i) reduction of Hg(II) in Arctic snow, both frozen and melted, is related to UV radiation intensity, with greater photoreduction of Hg(II) occurring at greater radiation intensities; and (ii) chemical species present in the snowpack, specifically chloride ions and DOC, will influence the rate and/or extent of Hg photochemical reactions in the snow.

2 Methods

2.1 Field Sampling

Surface snow (5-10 cm) was collected from three sites near the Polar Continental Shelf Program research base in Resolute Bay, NU, Canada (74.6975 ºN, 94.8322 ºW) from 8 – 12 March 2012 in late morning (Table A1.1). It should be noted that snow samples were more than 24 hours old, and no snowfall was observed over the course of our sample collection. Site 1 was located near the shore of a small ice covered pond, Site 2 was on the shaded side of a hill and Site 3 was located nearest to Resolute; sites were chosen to cover some general variation in snowpack cover and depth, and sampling locations (sunny, shaded or rocky) seen in the Resolute Bay area. Snow was scooped (acid washed plastic trowel) into and stored in 2.2L PTFE Teflon bottles (multiple Milli-Q water rinses) double bagged in Ziplocs® and sealed in dark coolers in a freezer (< -20 °C) until analysis. At each site, seven bottles of frozen snow (snow collected, shipped and stored without melting) and six bottles of melted snow (snow collected then melted in the dark and frozen for transport and storage) were sampled. A field blank was taken using an empty bottle for the same procedure and filled with MilliQ water to assess sampling and transport contamination, and Hg was found to be negligible (< 0.1 ppt).

2.2 Gross mercury photoreduction analyses

The rate of gross photochemical reduction of Hg in snow was determined in triplicate by irradiating samples in a sealed quartz vessel with constant intensity UV radiation (1.26 – 5.78 $W \cdot m^{-2}$), while flushing the sample with mercury-free “zero air”

(Tekran 1100) introduced at the bottom of the snow contained in the quartz beaker and monitoring the concentration of Hg(0) pumped from the sample through time (Fig. A1.2 – A1.7). Please see Fig. A1.1 for schematic of the experimental set up. For the gross reduction experiments, we assumed that photoproduced Hg(0) was removed as it formed by flushing the sample, thereby minimizing re-oxidation to Hg(II). In natural water systems, O'Driscoll et al. (2003) determined the fraction of photoproduced Hg(0) that could be removed from irradiated water at various temperatures using a similar experimental system; from that work a Hg(0) removal rate of ~ 3.5 $pmol \cdot L^{-1} \cdot h^{-1}$ can be approximated for the lowest temperature studied (4 °C). Assuming removal from snow will happen at an equal or greater rate, due to the low efficiency of Hg(0) interaction with ice surfaces (Bartels-Rausch et al., 2008; Ferrari et al., 2004a) and given that the rate of oxidation of Hg(0) in snow has been reported to be 0.5 – 0.7 $pmol \cdot L^{-1} \cdot h^{-1}$ (Fain et al., 2006), it can be assumed that Hg(0) will be removed before substantial oxidation has occurred in frozen or melted snow samples. It should be noted, however, some oxidation of Hg(0) may still occur, though the dominant Hg(0) removal mechanism should be evasion from the snow sample not photooxidation. Frozen snow was analyzed at -10 °C in a LuzChem photoreactor in a freezer and a range of UVA intensities were used to approximate the natural variation in Arctic spring insolation (Fig. A1.8 and A1.9). A high spectral transmission quartz beaker (300 mL; 2 mm thickness; QSI Quartz Scientific) was used as the sample chamber and was acid-washed (20% HCl) and pre-irradiated (UV) prior to analysis to ensure it was free of residual Hg. Laboratory measurements inside the photoreactor with and without quartz beakers found that the quartz beakers absorb 7.5%

of UVB and 12.6% of UVA radiation, however, reported UV radiation intensities have been corrected for this loss. The beaker was filled with snow to a height of 9 cm, weighed, and capped with an acid and Milli-Q cleaned silicon stopper. The Hg(0) in the interstitial pore space of the snow was removed by passing cold (-10 °C) mercury-free "zero air" through the foil covered sample (1 $L \cdot min^{-1}$) until Hg concentrations were below instrumental detection (<0.1 $ng \cdot m^{-3}$) for three consecutive readings using a Tekran 2537A cold vapor atomic fluorescence spectrometer (CVAFS). The snow was then UV irradiated (280 – 400 nm, 1.26 – 5.78 $W \cdot m^{-2}$; irradiation spectrum can be found in Fig. A1.8) with a single intensity of UV radiation, and simultaneous continuous gaseous elemental Hg analysis was performed (5 min resolution). Analyses were run until Hg(0) concentrations fell below the instrumental detection limit (0.1 $ng \cdot m^{-3}$) for at least 10 consecutive measurements. The amount of Hg released from each sample was mass-normalized to 200 g of snow. The rate constant (*k*) was determined by fitting the integrated form of a pseudo-first order reaction equation (Equation 3.1) to the scatter plot of cumulative Hg(0) versus time using SigmaPlot 12 software (O'Driscoll et al., 2006).

$$Hg(0) = Hg(II)_{red} \cdot (1 - e^{-k \cdot t}) \quad \text{(Equation 3.1)}$$

where Hg(0) is the cumulative amount of elemental Hg produced (pg) at time *t* (h), $Hg(II)_{red}$ is the total amount of photoreducible or photoreduced Hg (pg) and *k* is the pseudo-first order Hg reduction rate constant (h^{-1}). Note that "photoreduced" refers to the amount of Hg in the sample that has been reduced under given experimental conditions, while "photoreducible" Hg refers to the amount of Hg in a sample with the ability to be reduced under a given set of experimental conditions (i.e. chemical composition of the

sample and UV radiation intensity the sample is exposed to). That is to say, the photoreducible Hg is the amount of Hg that will be photoreduced in each experiment. Standard injections (n=10) of Hg(0) into the Tekran 2537, using a Tekran 2505 Hg vapour calibration unit and a Hamilton Digital Syringe (model 1702RN, 25UL), were performed at the beginning and end of the experiment to test Tekran 2537 recoveries. These recoveries were 99.7 ± 1.5 % and 98.4 ± 2.5% for the beginning and end, respectively. In addition, internal calibration of the Tekran 2537 was performed twice per month for the duration of the experiment.

Melted snow was stored as a frozen ice block in 2.2L Teflon bottles. This ice was completely thawed in the dark immediately prior to analysis to achieve a homogeneous sample. A 125 - 150 mL aliquot was weighed into the zeroed beaker and wrapped in foil. All Hg(0) was removed from the melted snow by bubbling mercury-free zero-air through the sample until Hg(0) was undetectable. The Hg(0)-free sample was then exposed to 1.26 – 5.78 $W \cdot m^{-2}$ UV radiation, with the exception melted snow from Site 1, which was exposed to 3.52 – 5.78 $W \cdot m^{-2}$ UV radiation due to low Hg(0) photoproduction. Mercury free zero air was bubbled through the sample at 1 $L \cdot min^{-1}$ for a 5 min sampling time and Hg(0) measurements made by a Tekran 2537. Analysis of gross Hg reduction in melted snow followed the procedure detailed by O'Driscoll et al. (2006) and Qureshi et al. (2010) for freshwater and ocean water samples, with the exception that the Luzchem photoreactor was held in a refrigerator at 4 °C, and a greater range of UV intensities were investigated (1.26 – 5.78 $W \cdot m^{-2}$).

2.3 Net mercury reduction and oxidation analysis

The rate constant for photooxidation of Hg in melted snow was determined as the difference between the net Hg photoreduction rate and the gross Hg photoreduction rate. In net photoreduction experiments Hg photooxidation has not been limited, and as a result both photoreduction of Hg(II) and photooxidation of Hg(0) occur at the same time in the beaker. To determine net Hg reduction, 12 beakers (11 treatments and one dark control) were filled without headspace and capped with silicone stoppers. Samples were irradiated for 0, 1, 2, 3, 5, 8, 12, 18 and 24 h and then analysed for Hg(0) content, that is, the net Hg reduction amount. At 12 h three beakers were removed for a triplicate analysis (average standard deviation = 6.8 pg Hg in 200g). To determine Hg(0) content, mercury-free zero air was bubbled through the irradiated samples and analysed with the Tekran model 2537, following Qureshi et al. (2010). The net reduction Hg(0) amounts were subtracted from the gross Hg(0) reduction amounts for each site, and these data were plotted. The result was the Hg oxidation curve, where rate constants can be derived as previously outlined, using Equation 3.2.

$$Hg(II) = Hg(0)_{ox} \cdot (1 - e^{-k_{ox} \cdot t}) \quad \text{(Equation 3.2)}$$

Where: $Hg(0)_{ox}$ is the amount of oxidizable Hg(II) present in the sample and k_{ox} is the pseudo-first order Hg oxidation rate constant.

2.4 Chemical characterization of frozen and melted snow

Melted snow from all three sites was analysed for total Hg, easily reducible Hg, pH, cations and anions, fluorescence and dissolved organic carbon (DOC). The pH was

determined using an Accumet basic model AB15 pH meter, and fluorescence was measured using a Turner model TD 700 fluorometer (excitation filter = 300 – 400 nm; emission filter = 410 – 600 nm). Easily reducible mercury (ERM), cations and anions, and DOC analyses were analyzed both pre-and post-irradiation (Fig. A1.10). Easily reducible mercury, or Hg that can be chemically reduced by stannous chloride addition, analyses were performed following the general procedure outlined by the US EPA method 1631 for total Hg in natural waters on a Brooks-Rand Model III system, without the use of bromine monochloride as a Hg oxidizing agent. Total Hg concentrations in non-irradiated samples were determined using the US EPA method 1631 with a Tekran 2600 system. Calibration standards, 5 ppt check standards and method blanks were run coincident with samples for quality control purposes. Detection limits, calculated as three times the standard deviation of blank measurements, were determined to be 0.15 ppt for total Hg and 0.02 ppt for ERM.

Dissolved organic carbon (DOC) was analyzed using a Shimadzu TOC-V CPH total organic carbon analyser. Samples were filtered through a 0.45 μm nylon syringe filter and frozen prior to analysis. Quality assurance check standards of 5 ppm organic carbon and 5 ppm inorganic carbon had good recoveries (>95%) in all analyses. DOC was plotted against UV intensity (Fig. A1.11), to determine the loss of DOC with irradiation in an effort to define the role of DOC in the photoreduction of Hg(II).

Samples for cation analysis (0.45 μm filtered and unfiltered samples) were acidified to 1% with HNO_3 for preservation and analysed using inductively coupled plasma mass spectrometry (Perkin Elmer Elan DRC). Samples for anion analyses (0.2 μm filtered)

were preserved by freezing then analysed using ion chromatography (Metrohm 850 Professional IC).

3 Results

3.1 Gross reduction

Rate constants (*k*) for gross Hg reduction in frozen and melted snow were determined in triplicate for each of the three sites. These values ranged from 0.11 to 0.60 h^{-1} for frozen snow (Fig. 3.1), and 0.08 to 1.05 h^{-1} for melted snow (Fig. 3.2). The gross Hg reduction rate constant showed a parabolic relationship with UV irradiation intensity while the amount of reducible Hg ($Hg(II)_{red}$) was linear with irradiation intensity (Figs. 3.1, 3.2) for all sites, except melted snow from Site 2, which had a linear reduction rate constant vs. UV intensity plot. Derivation of the rate constants and amounts of photoreduced Hg can be found in the supporting information (Tables A1.2, A1.3, A1.6, A1.7).

A positive linear relationship exists between the total divalent Hg reduced during the experiment ($Hg(II)_{red}$) and the intensity of UV radiation to which the frozen or melted snow was exposed (I_{UV}) (see Fig. 3.1; Tables A1.3 and A1.7). The amount of photoreducible Hg in the absence of UV radiation ($Hg(II)_{red,0}$), or the intercept value for $Hg(II)_{red}$ vs. UV intensity was less than zero in two of three cases, however, we caution against over-interpretation since these intercept values are not statistically significant in the majority of cases ($p > 0.05$). The slopes of the $Hg(II)_{red}$ vs. UV radiation lines are significantly different for the three sites ($p < 0.05$) and also for frozen versus melted

snow, except in the case of Site 1, where the difference is not significant ($p > 0.05$). This indicates differences in Hg reduction occurring in samples from the three sites, and also differences in the frozen and melted phases. Excluding melted snow from Site 2, which will be discussed later, Site 3 had slightly lower reduction rate constants for a given intensity of UV radiation compared to other sites in the same phase.

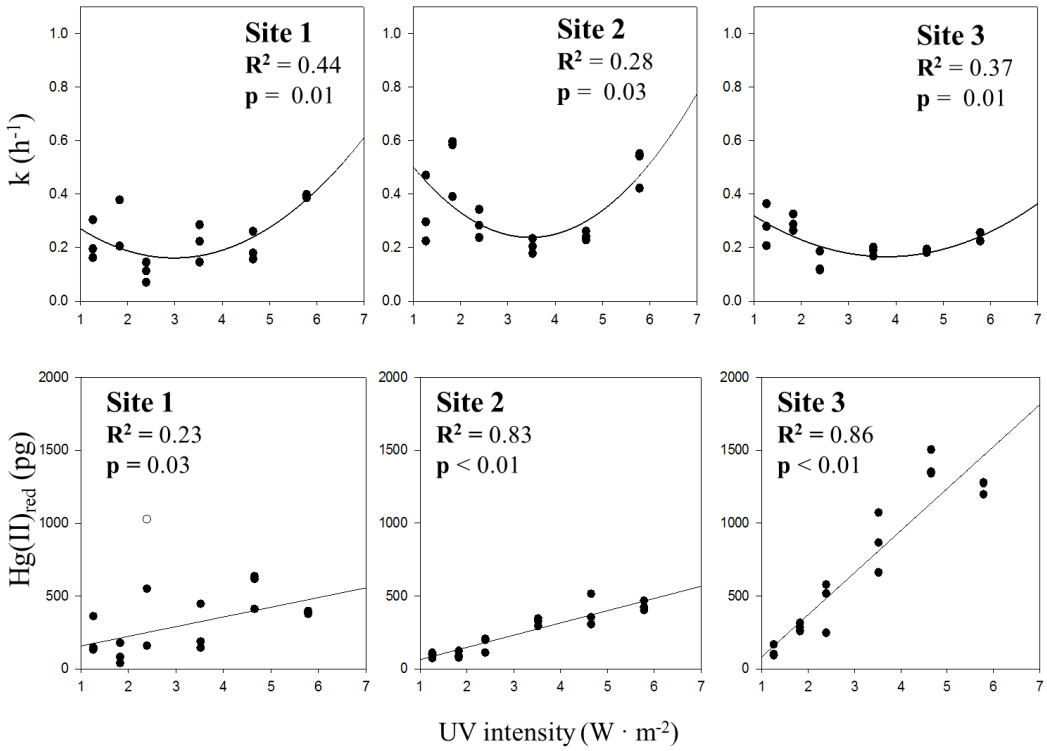

Figure 3.1: Plots of the pseudo-first order mercury photoreduction rate constant (k) and photoreducible mercury ($Hg(II)_{red}$) liberated from each frozen snow sample plotted against the UV (280 - 400 nm) irradiation intensity for samples from each site. Note that in the site 1 $Hg(II)_{red}$ vs UV intensity plot the open circle datum is an outlier not included in the linear regression.

The proportion of Hg that was photoreducible, determined as the percentage of total Hg that was photoreduced in each sample, was very different for different sites, and also for frozen and melted samples (Fig. 3.3), as was the percentage of easily reducible Hg that was photoreduced (Fig. A1.13). Melted snow from Site 2 had the highest percentage of photoreducible Hg, while both frozen and melted snow from Site 1 had

very little photoreducible Hg. In sites 1 and 3, frozen snow had more photoreducible Hg than melted snow.

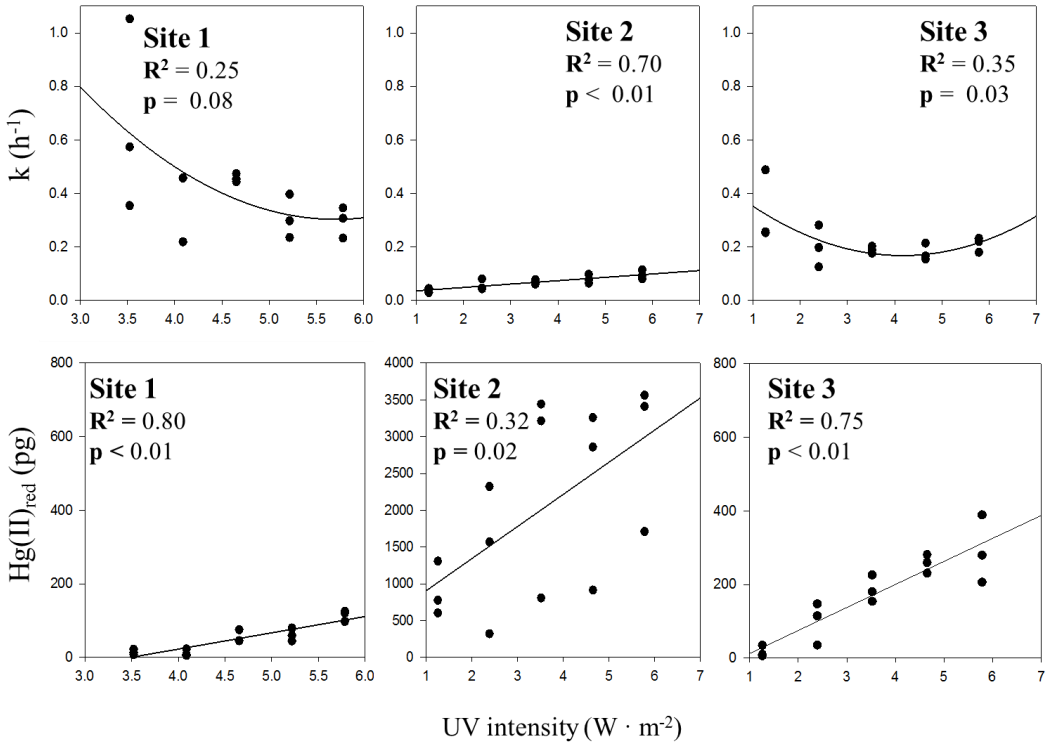

Figure 3.2: Pseudo-first order reduction rate constants (k) and total cumulative photoreducible mercury amounts ($Hg(II)_{red}$) for UV-irradiated melted snow from sites 2 and 3. Equations, coefficients and statistical significance for these plots can be found in the supporting information (Table A1.2, A1.3, A1.6 and A1.7). Note that the site 1 melted snow samples were exposed only to higher intensities of UV radiation (3.52 – 5.78 $W \cdot m^{-2}$), since lower intensities did not produce quantifiable levels of Hg(0).

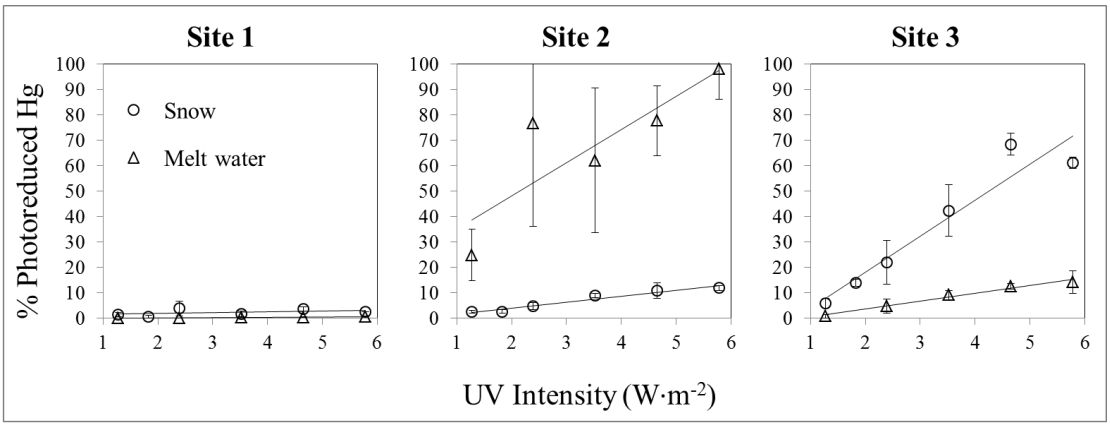

Figure 3.3: Percentage of the total mercury in a frozen (circle) or melted (triangle) sample that was photoreduced at a given intensity of UV radiation. Each data point is the average of a triplicate measurement, with error bars being plus/minus the standard deviation.

3.2 Oxidation of mercury in melted snow

Net Hg reduction was determined for melted snow from the three sites, to determine Hg(0) oxidation (Fig. 3.4). Site 2 had the greatest amount of Hg(0) oxidation (highest $Hg(0)_{ox}$; 2646 ± 773 pg in 200 g), with the lowest oxidation rate constant, k_{ox} (0.09 ± 0.02 h^{-1}), while Site 1 had the lowest $Hg(0)_{ox}$ (83 ± 7 pg in 200 g) and highest k_{ox} value (0.17 ± 0.08 h^{-1}).

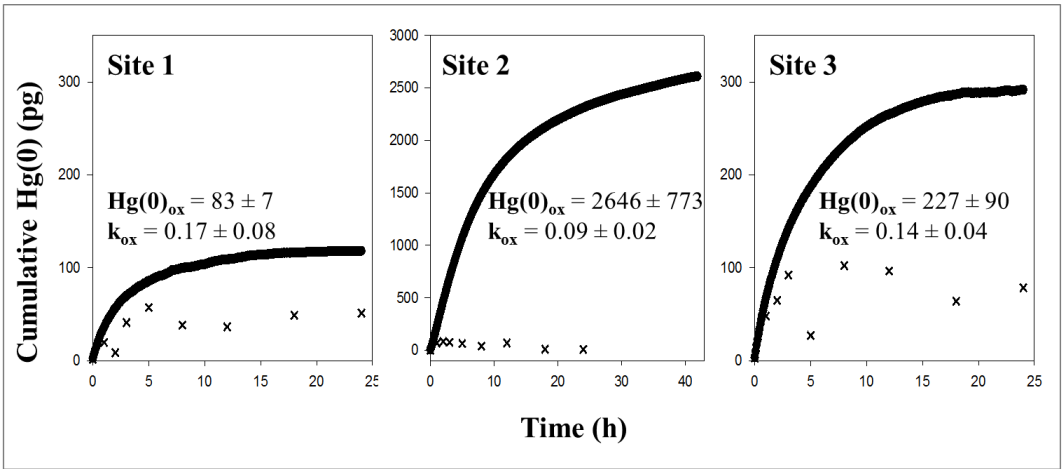

Figure 3.4: Gross (filled circles making up the solid black line) and net (x's) cumulative elemental mercury produced in melted snow irradiated with 5.78 W·m^{-2} UV radiation. Subtraction of the net from gross mercury reduction and subsequent curve fitting was used to determine mercury photooxidation rate constants for melted snow.

3.3 Chemical composition

The chemical composition of samples differed between sites. Site 1 had the largest concentration of total Hg (74 ppt) in non-irradiated snow, followed by Site 2 (18 ppt) and Site 3 (10 ppt). Site 1 also had the highest concentration of many ions, including chloride and iron, while Site 3 had the lowest ion concentrations (Fig. 3.5).

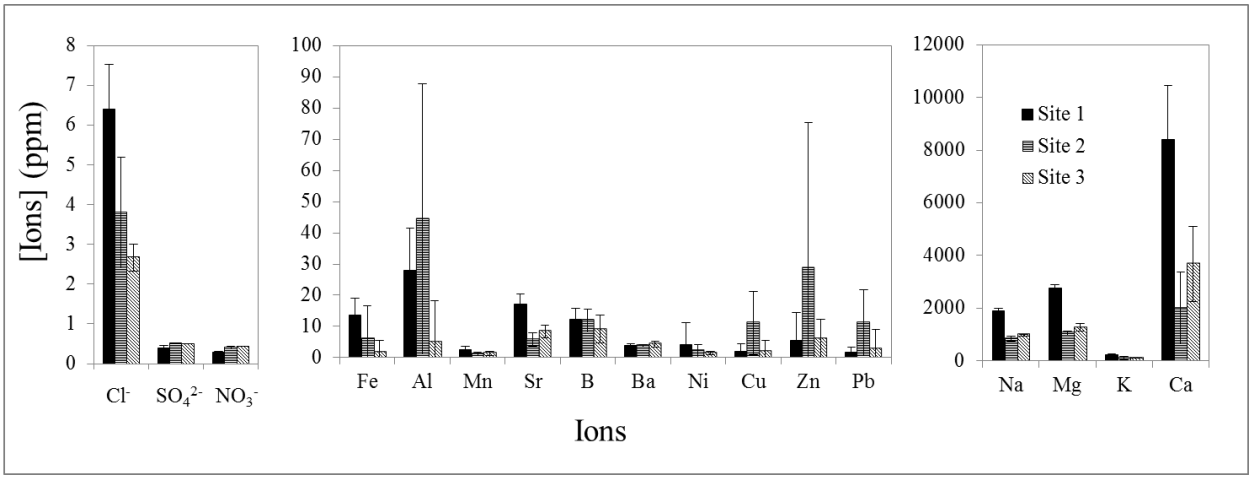

Figure 3.5: Concentrations of major ions found in irradiated frozen snow, given as the average ion concentration (n = 5) in all irradiated samples (all UV intensities), with error bars being the standard deviation of the ion concentrations for all irradiations at each site.

The concentration of dissolved organic matter, measured as dissolved organic carbon (DOC), decreased with irradiation of snow samples, with higher intensities resulting in greater photooxidation of DOC (1 – 50% loss of DOC with UV radiation from 1.26 – 5.78 $W \cdot m^{-2}$, respectively). This decrease was similar for all sites (Fig. A1.11). Overall, samples also had similar low initial DOC concentrations (0.64 ± 0.05 – 1.08 ± 0.20 ppm), with a wider variation of DOC concentration seen in the melted snow samples (Table A1.8). The pH of samples ranged from 4.22 ± 0.09 – 6.31 ± 0.26, with samples from Site 1 having higher pH values and Site 2 having lower pH (Table A1.8).

4 Discussion

Our results represent the first reported controlled photoreduction and photooxidation rates in frozen and melted Arctic snow, and their relationships with environmentally relevant UV irradiation intensity. However, many additional factors play a role in controlling Hg cycling in Arctic snowpacks, as can be seen by the variation in rate constants (k, k_{ox}) and amounts of photochemically available Hg ($Hg(II)_{red}$, $Hg(0)_{ox}$) in frozen and/or melted snow from different sampling sites. Chemical properties of the snow, pH, DOC, chloride and iron content, may all play a role in the determination of the rate of Hg photoreaction in an Arctic snowpack.

We hypothesize that the parabolic nature of the pseudo-first order Hg reduction rate constants with UV intensity, seen for frozen and melted snow, with the exception of melted snow from Site 2, suggests the presence of two pools of photoreducible Hg with different photolability. This idea of Hg with differing photolability has also been proposed by Qureshi et al. (2010) in ocean water and Pannu et al. (2014) in soils. We acknowledge that this parabolic relationship is stronger in some cases than others. In particular, melted snow for sites 1 and 3 do have lower k's at lowest UV intensity compared to highest UV (Fig. 3.2); however, parabolic relationships still provide better fits than linear relationships for these data. These results differ from those obtained for high Arctic lakes by Amyot et al. (1997), who found a linear relationship between photoinduced dissolved gaseous Hg production as a result of Hg(II) reduction, and the intensity of radiation received in liquid freshwater samples. In addition, Qureshi et al. (2010) examined Hg(II) reduction in sea water exposed to two intensities of UV

radiation, and found faster rate of Hg(II) reduction at the higher intensity. However, these studies did not use the lower intensities used in this work, which are more indicative of early springtime Arctic conditions. We propose that one photoreducible Hg pool is labile or easily photoreducible Hg and the second pool is a more recalcitrant photoreducible pool. We emphasise, however, that while we call it "recalcitrant" this pool of Hg is still photoreducible with adequate UV radiation. The presence of a refractory fraction of Hg in snow has also been proposed by Lalonde et al. (2002). The labile Hg(II) in snow would require very little radiation energy to be reduced to Hg(0) and would be reduced rapidly, even at very low UV intensities (high *k* at low UV; Figs. 3.1 and 3.2). The recalcitrant Hg pool would require more radiation energy to be reduced to Hg(0), so at mid-range UV intensities, photoreduction of the recalcitrant pool would be slow, while photoreduction of the labile pool would still be fast. At these mid-range intensities, the rate dynamics would be largely controlled by the more recalcitrant pool, which is thought to be present in higher amounts, resulting in a combined *k*-value lower than would be obtained from the labile pool alone (low *k* at mid-range UV). At higher UV intensities the more recalcitrant pool will be reduced more quickly due to the availability of higher energy photons, again largely controlling the rate dynamics (high *k* at high UV). It should be noted that in freshly fallen snow, labile Hg has been proposed to dominate snowpack Hg (Lalonde et al., 2002); however, the snow collected in this work was more than 24h old, which may have allowed loss of some of the labile Hg prior to collection, since more than 50% of Hg in snow may be lost within 24h (Lalonde et al., 2002).

Differences in the photochemical behaviour of Hg seen in frozen versus melted snow are hypothesized to be due to the exposure of Hg(II) to more or different binding groups of DOC, altering the photolability of that bound Hg(II) when the snow melts. In frozen snow, higher levels of photoreduction of Hg(II) occurred coincident with a greater loss of DOC. In freshwaters, similar losses of DOC with irradiation are seen (Haverstock et al., 2012; O'Driscoll et al., 2006, 2004; Weber, 1993). In contrast to frozen snow, melted irradiated snow showed less photooxidation of DOC with increasing UV radiation intensity, that is, higher DOC concentrations were observed for higher UV irradiation intensities (75% - 10% loss of DOC for 1.26 – 5.78 $W \cdot m^{-2}$, respectively). Increases in DOC have been observed with the irradiation of fresh and marine water samples, due to breakdown of particulates by solar radiation (Pisani et al., 2011; Shank et al., 2011), and may explain the reduced net loss or photooxidation of DOC with higher UV intensity in the melt water. The difference in DOC-Hg reduction relationship may also imply a difference in the role of DOC in frozen compared to melted snow of the same chemical composition. The positive relationship between DOC photooxidation (loss) and Hg(II) photoreduction with increasing UV irradiation may mean that photooxidation of DOC enhanced or allowed photoreduction of Hg in the frozen snow samples. This positive relationship was not observed in the melted snow samples, which suggests DOC photooxidation did not act to enhance Hg(II) reduction in melted snow. It is, however, possible that DOC functional groups will not behave in snow as they do in natural waters, as a result of differences between these two media, and so, lacking chemical speciation of DOC functional groups in snow, these are simply hypotheses. It should be noted that

radiation transmission will also differ in frozen and melted samples, which could further influence Hg photoreduction in these two types of samples. However, using the spectroradiometer we determined that UV radiation from the photoreactor bulbs completely penetrated both frozen and melted snow samples.

The differences in the rates and extents of Hg photoreactions between sites may be partially attributed to differences in the chemical composition of the snow, in particular iron and chlorine concentrations (Mann et al., 2014). Snow from Site 3 had the lowest concentrations of iron and chloride (Fig. 3.5). Other research has shown that increasing chloride ion concentration favours photochemical oxidation over reduction of Hg in snow (Amyot et al., 2003; Lalonde et al., 2003). Although the role of iron in snow photochemistry is unexplored, research shows that ferrous iron increases Hg reduction in natural waters in the presence of DOC by producing radicals which can quickly reduce Hg(II) and potentially increase the overall rate of reduction (Deng et al., 2009; Lin and Pehkonen, 1997; Zhang and Lindberg, 2001). We posit that low concentrations of chloride ion in Site 3 may have increased the extent of photochemical reduction of Hg, relative to the other site samples, due to the presence of fewer Hg-chlorocomplexes, leading to higher $Hg(II)_{red}$ values (Fig. 3.1, 3.2) and % photoreduced (Fig. 3.3) at each intensity of incident UV radiation. In addition the higher iron concentrations in site 1 and 2 snow may increase the rate of Hg photochemical reduction, giving rise to the higher pseudo-first order reduction rate constants, *k,* observed relative to Site 3.

The unique Hg reduction kinetics observed in the melted snow samples from Site 2 suggest the possibility of interactions with other factors such as particulates and

differences in chemical composition of the quasi liquid layer in frozen snow and bulk melted snow. The melted snow from Site 2 exhibited a linear increase in *k* with UV intensity, and also had much larger $Hg(II)_{red}$ values in comparison with sites 1 and 3. These differences may have arisen due to: (i) a change in surface reactions with melting, due to the availability of particulates in the bulk aqueous phase of the melted snow; or (ii) differences in the chemical species or concentrations available in the melted snow versus the quasi-liquid layer of the frozen snow, as a result of ice crystal melting or soluble portions of particulate matter in snow dissolving in snowmelt.

We suggest Site 2 melted snow lacked the easily photoreducible Hg pool present in the other samples and this may be related to the availability of particulate matter. Particulate matter in the interior of the snow grains will be isolated from the quasi-liquid layer on the surface, where most snow reactions are thought to take place (Ferrari et al., 2005; Jacobi and Hilker, 2007; Sherman et al., 2010). Large particles, which would be continuously suspended during photoreduction experiments in melted snow due to the aeration of the sample during analysis, could provide surfaces for Hg photochemical reactions, thus changing photoreduction rate and extent. However, filtering through a 0.45 μm nylon syringe filter, prior to irradiation did not significantly change the rate or extent of gross Hg reduction ($t = 0.14$, $p = 0.28$), so surface reactions with large particles do not appear to be important.

Alternatively, it is possible is that soluble portions of the particulates may dissolve when snow is melted and modify the chemical composition of the melted snow, by adding ions like chloride, or modifying DOC-Hg interactions in the bulk liquid compared

to the quasi-liquid layer of snow, thereby changing the relative amounts of easily photolabile and recalcitrant Hg, or simply by adding additional soluble Hg(II) species. Currently there is no reliable method for quantifying DOC-Hg binding structures in the quasi-liquid layer of snow, so it is not possible to compare bulk liquid chemistry and that of the quasi-liquid layer. As such more research is needed to test this hypothesis.

In addition to the linear relationship between reduction rate constants and UV radiation in melted snow from Site 2, extremely high $Hg(II)_{red}$ values were also found in samples from this site, relative to all other experimental conditions. This could mean that less Hg was sorbed to particles following melt, and likely more available to be photoreduced, resulting in higher $Hg(II)_{red}$ values due to moderate chloride and low pH conditions in the bulk melted snow (Fig. 3.5 and Table A1.8). Mann et al. (2011) determined that when laboratory-synthesized snow was acidified and spiked with NaCl, more Hg was present in the dissolved phase than in lab-synthesized neutral snow containing no NaCl. Conversely, Lalonde et al. (2003) and Amyot et al. (2003) found that chloride promotes Hg photooxidation and/or inhibits Hg photoreduction, which would imply that the observed differences in reduction behaviour of melted snow cannot be solely explained by increased chloride content.

The research presented here has significant implications for the modelling of Hg fate in Arctic ecosystems. Changing climate conditions in the Arctic have led to a depletion in stratospheric ozone and an increase in the levels of UV radiation reaching the surface in Arctic regions (Frederick, 1993; McKenzie et al., 2011; Nishioka et al., 2010). Our work suggests that changing UV conditions will influence both the rate and extent of Hg

photoreduction in Arctic snow, as predicted by the parabolic relationship observed between *k* and UV intensity (Figs. 3.1 and 3.2). Furthermore, increasing temperatures are resulting in thinner sea ice and a shorter duration of annual ice cover over the Arctic Ocean (Comiso, 2006; Kattsov et al., 2005; Meier et al., 2007; Rothrock et al., 1999). With thinner ice and more open water, the chloride ion content of atmospheric particles in the Arctic will likely increase, which may further affect Hg behavior in the snowpack. In addition, changing climate conditions may influence AMDE dynamics as a result of changing sea ice coverage (Moore et al., 2014). Snow and firn near sea ice leads can have Hg concentrations reaching 820 $ng \cdot L^{-1}$ (Douglas et al., 2005), and this work suggests lower extents of Hg(II) photoreduction in snow with higher chloride concentrations (e.g., in snow from Site 1), as was also shown by Steffen et al. (2013). Collectively, these conditions could result in higher inputs of Hg(II) to receiving water bodies in the spring as snow melts, which may lead to greater MeHg production in Arctic environments (Mason and Sheu, 2002).

5 Conclusions

Our study provides the first determination of the kinetics of Hg photoreduction and photooxidation in Arctic snow and snowmelt (three sites in Resolute Bay NU, Canada) and relationships with UV radiation intensity and snowpack chemistry. The Hg photoreduction rate constants showed a parabolic relationship with UV radiation intensity, while amounts of photoreduced Hg increased linearly. This suggests that volatile Hg will be created quickly at both low and high radiation intensities, but the

majority of the Hg in the snowpack will be reduced at high radiation intensities. We also found differences in the rate and extent of Hg(II) photoreduction and Hg(0) photooxidation in frozen and melted snow, which may be attributable to differences in the chemical nature of the samples. In particular, differences in DOC, chloride and iron availability may drive some of these variations. These fundamental measurements are key to the development of predictive models describing Hg retention in Arctic ecosystems with a changing climate and suggest that increased radiation levels in the Arctic may have substantial implications for Hg retention in snow.

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CHAPTER 4: MERCURY LOSS FROM ARCTIC SNOW IS CONTROLLED BY UV IRRADIATION, TEMPERATURE, AND SNOW AGE

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Abstract

Mercury (Hg) is an important environmental contaminant, due to its neurotoxicity and ability to bioaccumulate. The Arctic is a mercury-sensitive region, where organisms can accumulate high concentrations of Hg. The Arctic is also a region experiencing rapidly changing environmental conditions, including increased ice and snow melt. The extent to which Hg moves with meltwater may be largely controlled by snowpack mercury photo-redox reactions. The aims of our work were: 1) to determine the significance of environmental conditions (temperature, UV irradiation, and snow age) on Hg(0) flux from Arctic snow, and 2) to elucidate the importance of temperature on snowpack Hg reduction kinetics. We used a Teflon flux chamber erected in the high Arctic, and found that snow temperature, UV irradiation and snow age were significant variables controlling Hg(0) flux from Arctic snow. Cross correlation analysis determined that Hg(0) flux lagged UV irradiation by 5 min and snow temperature by 30 min, indicating that UV radiation has a direct effect on Hg(0) flux, while temperature may indirectly influence the flux. Controlled laboratory experiments determined that temperature influenced Hg photoreduction kinetics when snow approached the melting point (>-2 °C). At these temperatures, the pseudo-first order reduction rate constant, *k*, decreased approximately two-fold, and the total photoreduced Hg amount, $Hg(II)_{red}$, increased ten-fold, relative to lower temperatures. This result suggests that temperature influences Hg photoreduction kinetics indirectly, likely through alteration in the ratio of solid: liquid water in the snowpack and associated changes in the mobility/availability in reactants. These results imply that large mass transfers of Hg from snow to air may take place

during the spring Arctic snowmelt period, thereby altering photoreducible Hg retention and transport with snow meltwater.

1 Introduction

1.1 Mercury speciation and Arctic mercury implications

Mercury (Hg) exists in three main environmentally relevant forms: elemental (Hg(0)), divalent (Hg(II)) and organic methylmercury (MeHg). Elemental Hg is volatile and relatively insoluble (Clever et al., 1985), existing primarily in the gas phase, with a typical atmospheric lifetime of ~0.5-2 years (Holmes et al., 2006; Lindqvist and Rodhe, 1985). Hg(II) is found primarily in condensed phases in the atmosphere, and is deposited to the Earth's surface, but also exists in the gas phase. Reactive gaseous mercury (RGM) is an operationally defined form of atmospheric Hg thought to be primarily gas phase Hg(II), with an atmospheric lifetime of a few hours (Holmes et al., 2009) to a few days (Dastoor et al., 2008). Newly deposited Hg ihas been proposed to be bioavailable to bacteria, and might be more readily methylated than previously existing Hg(II) (Lindberg et al., 2002). In addition, Hg deposited with snow might be more bioavailable than Hg deposited with rain (Scott, 2001), making snowpack Hg dynamics very important from an ecosystem health perspective. The majority of Hg in a snowpack exists in condensed phases, with < 5% as Hg(0) in the snow interstitial air (Dommergue et al., 2003; Ferrari et al., 2004). Methylmercury is the species of greatest concern from an organism health perspective, since it is a neurotoxin and can bioaccumulate and biomagnify (Ekino et al., 2007).

The Arctic is a region where Hg contamination is particularly problematic. Upper trophic level predators (marine mammals and birds) tend to accumulate high concentrations of Hg and this Hg can be passed on to humans who consume them (Carrie et al., 2010; Ford, 2009; Kirk et al., 2012). The Arctic is also a region where the Hg cycle is particularly dynamic, especially in spring. Atmospheric mercury depletion events (AMDEs) are large-scale Hg deposition events that occur during polar spring and display atmospheric Hg(0) concentrations <1 ng/m^3 (Schroeder et al., 1998). The majority of Hg deposited to snow with AMDEs is thought to be RGM as opposed to particle bound Hg (PHg) (Brooks et al., 2006), although the relative fraction of RGM to PHg varies, and PHg may be the dominant form of Hg(II) deposition in some cases (Larose et al., 2011; Steffen et al., 2013). Since deposited RGM species are photochemically active, they are subject to reaction and reemission from snow (Dommergue et al., 2010). It has been determined that 4 – 7% of this AMDE deposited Hg is "easily" reducible, and quickly lost as Hg(0) (Johnson et al., 2008); however, up to 90% of the AMDE deposited Hg may be lost within 1 to 2 days (Poulain et al., 2004).

The snowpack is the main source of Hg to Arctic wetlands (Loseto et al., 2004) and much of the Hg deposited to snow may be bioavailable and move with snow melt (Larose et al., 2011; Lindberg et al., 2002). At the onset of melt, most of the remaining Hg(II) in the snowpack is quickly eluted and concentrated in the first fractions of the snow meltwater, resulting in a pulse of bioavailable Hg(II) to water bodies early in the melt period (Dommergue et al., 2010; Lindberg et al., 2002). Particle bound Hg (PHg) species is retained by the melting snowpack until the last of the snow has melted (Dommergue et

al., 2010; Mann et al., 2011). Overall, this means Hg remaining in snow may be a key factor in regulating Hg entering aquatic food webs, given its potential to move with meltwater.

1.2 Mercury snowpack photoreactions and flux

Mercury (Hg) is deposited to the snowpack as a part of wet and dry deposition, with deposition of RGM and PHg being more efficient than GEM, and roughly equivalent amounts of Hg deposited by wet and dry deposition (Lin et al., 2006), although dry deposition is not well constrained. Once present in the snowpack, Hg is very labile, changing speciation (Lalonde et al., 2002; Schroeder and Munthe, 1998) and having the potential to undergo dynamic exchange with the atmosphere (Dastoor et al., 2008; Ferrari et al., 2005; Kirk et al., 2006; Steen et al., 2009). Photochemical reactions are important for altering the speciation of Hg in a snowpack (Durnford and Dastoor, 2011; Mann et al., 2014; Poulain et al., 2004). Photoreduction of Hg(II) in snow forms Hg(0), which is volatile and does not sorb appreciably to ice crystals (Bartels-Rausch et al., 2008; Ferrari et al., 2004), allowing Hg(0) to move back to the atmosphere by diffusion with concentration gradients (Albert and Shultz, 2002; Ferrari et al., 2004), or by snowpack ventilation (Faïn et al., 2013; Ferrari et al., 2005). Flux of Hg(0) from Arctic snow has been measured and proposed to be related to solar radiation, with coinciding maximum solar radiation intensities and fluxes (Dommergue et al., 2010; Faïn et al., 2007; Ferrari et al., 2008; Lahoutifard et al., 2005). Mann et al. (2015) determined that the kinetics of Hg photoreduction in Arctic snow are related to UV radiation

intensity, with higher UV intensities resulting in more Hg in snow being reduced to Hg(0), while the rate of Hg photoreduction is greatest at both low and high UV intensities. Further environmental parameters, like temperature, have been discussed; however, the dependence of Hg flux on temperature remains unclear.

1.3 Temperature dependence of mercury photoreactions

Temperature may influence snowpack reactions in two general ways: by directly affecting the kinetics of chemical reactions, or by modifying the fraction of solid: liquid water present, affecting reactant availability and reactivity. Specifically, temperature may also alter the microstructure of snow, altering surface area and so affecting Hg reaction kinetics if photoreactions are surface-type reactions in the QLL (Jacobi et al., 2007). There is no present consensus in other studies regarding the interaction of solar radiation and temperature on Hg reduction kinetics in snow. Dommergue et al. (2007) determined that in the absence of radiation, temperature had a negligible effect on Hg(0) production in snow. However, Steffen et al. (2002) found that in the field with solar radiation present, temperature could play an important role in determining Hg(0) production in and emission from snow, with warmer temperatures sometimes leading to greater Hg(0) emissions. Lahoutifard et al. (2005) concluded that temperature was one of the key factors in determining the net deposition or volatilisation of Hg in snow, and Fain et al. (2007) concluded that temperature and solar radiation were the main environmental parameters controlling Hg(0) production in snow interstitial air. Ferrari et al. (2005) reported that Hg(0) production in snow appeared to be related to temperature, and while

temperature was not proposed to be directly controlling Hg(0) production it was concluded that temperature plays a key role in the photoproduction of snowpack Hg(0). Steen et al. (2009) suggested that Hg(0) emission from snow is more favourable than deposition at some temperatures , although air temperature was not strongly correlated to snowpack Hg(0) emission or deposition during their study. Temperature may influence Hg reactions by altering the fraction of Hg that is susceptible to photoreactions. As temperatures increase towards melting, a greater fraction of Hg in snow may exist in "stable" forms that may result from sorption to particles or microbial action (Ferrari et al., 2008). The change in the relative amount of stable Hg could then influence the rate and extent of Hg photoreactions with varying snow temperature.

It is clear that while many researchers have attempted to describe the influence of temperature on Hg behaviour in snow, a consensus is lacking, possibly due to variability in research design. In particular, temperature is often not isolated from other environmental factors when determining relationships. In addition, studies have relied largely on *in situ* field data alone, making it difficult to isolate individual factors changing Hg reactivity in snow. Since temperature is a critical factor in Hg speciation and reactivity in other media (Pannu et al., 2014), we hypothesized that increasing temperature would increase the rate and magnitude of Hg photoreactions and Hg(0) release (flux) from Arctic snow exposed to constant UV intensity. This hypothesis was tested using two methods: 1) a Teflon flux chamber *in situ* to quantify the flux of Hg(0) from snow with incident solar radiation and temperature measurements to determine whether temperature affects Hg(0) flux from Arctic snow, and 2) a temperature-

controlled laboratory method (Mann et al., 2015) to determine whether Hg(II) reduction kinetics in Arctic snow change with varying temperature.

2 Methods

2.1 Flux chamber set up and use

Flux of Hg(0) from snow was measured from 20-28 March 2013 at Resolute Bay, NU, Canada near the Polar Continental Shelf Program research base (74.6975 ºN, 94.8322 ºW) using a chamber method. To measure Hg flux from the snowpack, a clean, blanked rectangular Teflon chamber was used, as detailed by Carpi and Lindberg (1998) for soil Hg(0) flux, Beauchamp et al. (2002) for terrestrial and freshwater Hg(0) flux, and O'Driscoll et al. (2003) for freshwater water Hg(0) flux. This chamber covered a 58 x 20 cm area of snow, and the edges of the support base were covered with weights and snow, effectively isolating the interior of the chamber from future atmospheric deposition. Air from inside the flux chamber was sampled at 1.5 L min^{-1} for two consecutive 5 min Hg(0) analysis intervals, followed by two consecutive 5 min measurements of ambient Hg(0) concentration. Hg(0) was quantified by a Tekran 2537B instrument, with a Tekran model 1110 synchronized two-port sampler used to switch between sampling of ambient and chamber air. Ambient air was sampled at the same height as the chamber air, approximately 15 cm from the snow surface. A Gast model DOA-P104-AA pump and Bios Definer 220-M mass flow meter were used to maintain 1.5 L/min of air flow through all sample lines at all times to prevent stagnation in the chamber. The difference between a consecutive chamber and ambient Hg(0) concentration was used to express

Hg(0) flux from the snow surface. Instruments were placed inside a dome-shaped canvas tent heated with a propane heater to maintain proper function. The flux chamber was placed on four individual plots of clean, undisturbed snow (sites A – D), and Hg(0) flux was measured for 2 – 3 d at each site. All sites were within 2 – 3 m of each other, and no site was sampled twice. Snow under the flux chamber was 16 – 29 cm deep, with the greatest depth at site D as a result of continued snowfall during the sampling period.

Concurrent with *in situ* Hg(0) flux determination, the intensity of incoming solar radiation was quantified using an OceanOptics USB 4000 spectroradiometer with a fibre-optic probe. The spectroradiometer probe was fastened to the outside of the frame supporting the chamber at 20 cm above the snow surface. The probe was not placed inside the Teflon chamber to prevent contamination of the interior of the chamber, and to ensure the chamber was sealed from ambient air; however, there is ~12% loss of UV radiation through the flux chamber, as measured in the lab.

Temperature was monitored in both snow and air. Surface snow temperatures were measured using HOBO Pendant® temperature/alarm data loggers buried ~5 – 10 cm beneath the surface, and air temperatures were measured ~2 m above the snow surface using a Davis Vantage PRO 2 weather station. Temperature measurements were recorded every 5 or 10 min for the duration of the flux measurement period.

2.2 Snow sampling

Snow was collected during the flux chamber deployment for the controlled laboratory experiments. Clean 2.2L Teflon® bottles were filled with surface (5 to 10 cm)

snow collected near the flux measurement site using an acid washed plastic trowel. The snow sampling location was selected out of the immediate vicinity of the flux chamber to avoid disturbing the flux measurement site. Clean suits were worn during snow collection to prevent contamination, and samples were stored outside, frozen in dark, sealed coolers, then shipped, frozen back to Acadia University for analysis.

2.3 Temperature dependence of Hg photochemical reduction

The rate and extent of Hg photoreduction in snow were determined following the methods of Mann et al. (2015). Briefly, ~90g of snow was placed in a sealed, acid washed and pre-irradiated quartz beaker and flushed with Hg-free zero air in the dark to remove existing Hg(0). Snow was then irradiated with 4.65 $W \cdot m^{-2}$ UV radiation for ~24 h in a LuzChem photoreactor held at a constant temperature in a walk in freezer, while Hg-free zero air was pumped into the bottom of the beaker, and headspace above the snow was sampled at 1L min^{-1}. Maximum midday UV intensity measured in Resolute Bay, NU in March 2013 ranged from ~5 to 15 $W \cdot m^{-2}$ (Fig. 4.1), making our laboratory irradiations the lower end of maximum UV intensities observed in the field. Hg(0) in the headspace was quantified using a Tekran 2537A Hg vapour analyser. Resulting amounts of cumulative Hg(0) evolved were plotted against time, and pseudo-first order kinetic equations fit to determine the reduction rate constant, *k*, and the total photoreduced Hg amount, $Hg(II)_{red}$ at each temperature (Equation 4.1). To determine the influence of temperature on *k* and $Hg(II)_{red}$, the temperature was varied between -2 and -20 °C, with

triplicate trials at each of six temperatures. When the temperature was changed, instruments were left to equilibrate for 4 to 8 h prior to beginning a trial.

$$Hg(0) = Hg(II)_{red} \cdot (1 - e^{-k \cdot t}) \quad \text{(Equation 4.1)}$$

2.4 Analysis

Graphs were used to provide summary trends in flux UV intensity and temperature relationships. Cross correlation analyses were used to determine time lags between measured Hg(0) flux changes, UV intensity and snow temperature. The relationship between temperature, snow age and Hg(0) flux from snow was modeled using a Generalised Additive Model (GAM) (see Zuur (2012) for more information) with Hg(0) flux as the response variable and UV intensity as an offset. An offset is a variable that represents 'effort' or 'rate' and the model takes into consideration the influence of this offset on the response variable before determining the significance of the other variables. In our case with an offset of UV intensity, the response would then be similar to the Hg(0) flux per unit UV intensity, and the significance of the influence of snow temperature and snow age on Hg(0) flux per unit UV could be determined. Smoothers were included for variables that showed non-linear relationship with the response variable (snow temperature and snow age) and their exclusion tested against the full model. All analyses were conducted using R software (R Core Team 2014, version 3.1) within RStudio (version 0.98.1062).

3 Results and Discussion

3.1 Flux

In the field data (Fig. 4.1) we observed that Hg(0) flux from snow increased from 0 to 7 $ng \cdot m^{-2} \cdot h^{-1}$ with increasing UV radiation intensity (0 to 13.8 $W \cdot m^{-2}$), with both flux and UV peaking at midday. In addition, snow temperature displayed a diurnal pattern, with maxima at midday, when both flux and UV are highest. It cannot be determined from visual examination alone whether temperature influences Hg(0) flux, or if both are independently influenced by UV radiation. We found that flux lagged UV radiation intensity by ~5 min, while flux lagged snow temperature by ~30 min (Fig. A2.1, A2.2). The 5 min lag between a change in UV intensity and flux of Hg(0) from snow likely represents a near immediate change in flux as a result of UV changes since flux measurement was obtained every 10 min, but UV radiation intensities were recorded every 5 min. This indicates that UV radiation directly influences the kinetics of Hg reduction in the snowpack with the rate or extent of Hg(II) photoreduction changing based on the intensity of UV radiation available. Mann et al. (2015) determined that UV radiation significantly influences the rate and extent of Hg reduction in Arctic snow, which supports this conclusion based on cross correlation analysis. In contrast, the 30 min lag between a change in snow temperature and a change in Hg(0) flux indicated that changes in snowpack temperature do not result in instantaneous changes to Hg(0) flux from snow. This lag suggests that temperature may not directly influence the photoreduction of Hg(II) in the snowpack. It is likely that temperature influences the relative ratio of solid: liquid water in the snowpack, which may alter the availability of

reductants needed to allow Hg(II) to undergo photoreduction in snow, by increasing molecular mobility; however, there was no visible melt of the snow inside the chamber over the course of irradiation.

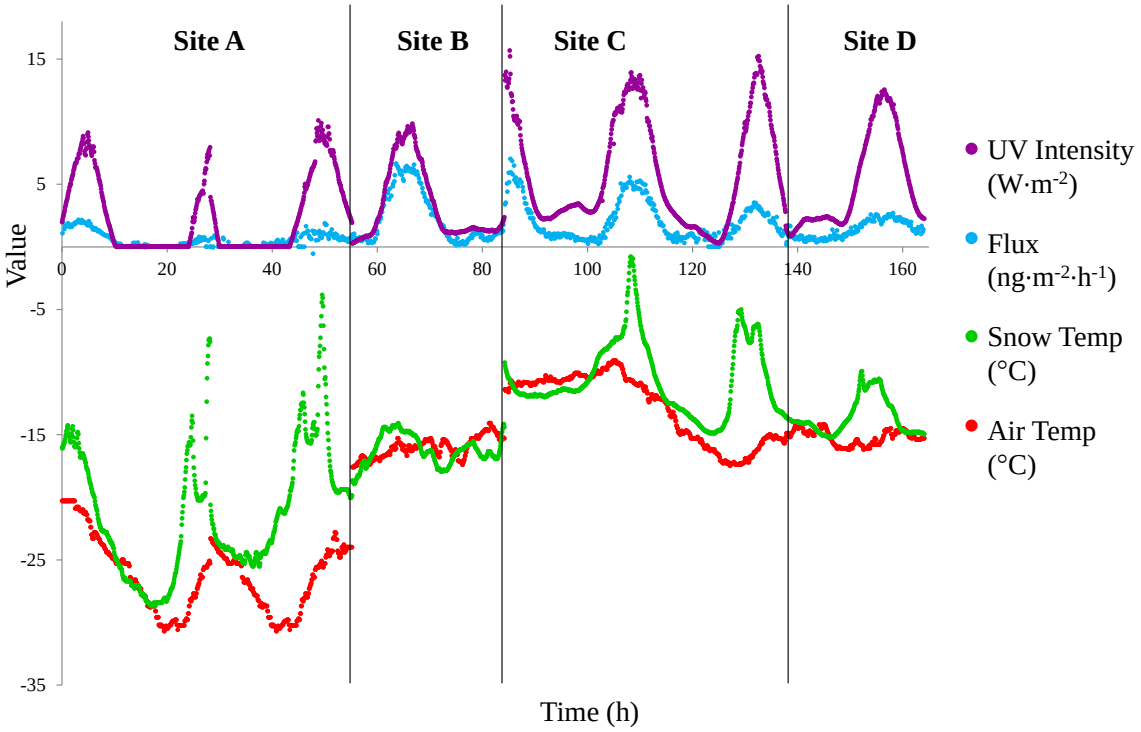

Figure 4.1: Incoming solar UV (280 – 400 nm) radiation, Hg(0) flux, snow and air temperatures measured 20 – 28 March, 2013 at Resolute Bay, NU, Canada. Note that time is shown in hours as continuous, but there are time breaks occurring at each vertical black line (when the chamber was moved).

In the field, we observed that the longer the chamber covered a plot of snow, the smaller the maximum Hg(0) flux at midday (Fig. 4.1; Fig. A2.3). By separating the flux and UV intensity data based on snow age and plotting the slopes against the duration since the experiment began, we found that approximately 5 d after surface snow was isolated from the atmosphere by covering with a Teflon flux chamber, Hg(0) emission fluxes would be ~0 $ng \cdot m^{-2} \cdot h^{-1}$ (Fig. A2.4, A2.5). We hypothesized that the age of snow may influence the amount of available photoreducible Hg in surface snow and may also

be an important variable influencing Hg(0) flux from Arctic snow, since the chamber isolates the covered snow from new atmospheric Hg inputs. Snow age and temperature were tested to determine their significance, by including each as a "smoother" in the GAM (Equation A2.1). Previous research has shown that solar radiation significantly influences Hg flux from snow (Dommergue et al., 2010; Faïn et al., 2007; Ferrari et al., 2008; Lahoutifard et al., 2005; Mann et al., 2015); therefore radiation was included in the GAM as an offset. An offset was included to weight or normalise Hg(0) flux by radiation, essentially removing the influence of UV radiation in the model and allowing the influence of temperature on Hg(0) flux to be determined. We found that snow temperature significantly ($p < 0.05$) influenced the flux of Hg(0) from snow as did the age of the snow under the chamber ($p < 0.05$). Overall, the GAM was able to describe 77.3% of the variability observed in the Hg(0) flux from snow values, over the course of the field campaign (Fig. A2.6). It should be noted that the GAM predicts deposition fluxes during the night (Fig. A2.7), but this was not observed in the field. This may mean that Hg(0) deposition was possible but not observed, perhaps due to isolation from the surrounding atmosphere, or due to the removal of Hg(0) as the air above the snowpack is sampled to determine flux, but probably is just a function of the model not fitting the data perfectly. When the temperature smoother was excluded, the model performance decreased, explaining 62.5% of the variability in the field flux data. This shows that temperature is an important factor in determining the flux of Hg(0) from Arctic snow ($p < 0.05$), but it does not appear to be the most important factor.

3.2 Temperature

Since field experiments showed that temperature significantly affects Hg(0) flux from snow, controlled laboratory experiments were performed to further investigate the relationship. In the lab temperature does not appear to influence Hg photoreduction kinetics in a statistically significant way until snow approaches the melting point (at -2 °C air temperature during irradiation) (Figs. 4.2 and 4.3). Rate constants did not significantly ($p > 0.05$) change between -20 °C to -5 °C and total photoreduced Hg amounts showed no consistent pattern with these temperatures. During irradiation at -2 °C, snow in the photoreactor melted completely within 1 to 2 h, indicating that temperature within the quartz beaker was at ~ 2 °C higher than ambient freezer air. No visible melted fraction or reduction in snow volume (that would indicate partial melt) was observed during any other temperature trials. Under the -2°C freezer conditions, a higher evasion of Hg(0) from the sample was observed (larger $Hg(II)_{red}$ value for -2 °C). Fain et al. (2007) also observed a spike in GEM emissions when alpine snow melted, and Dommergue et al. (2003) determined that peak Hg(0) emission from snow coincides with snow melt. As the snow melts, the quasi-liquid layer (QLL), the region where snow reactions are thought to occur (Ferrari et al., 2005; Jacobi et al., 2007; Sherman et al., 2010), increases in size. This could mean greater potential for Hg(II) to come into contact with reductants, thereby increasing the extent of Hg(II) photoreduction (Faïn et al., 2007).

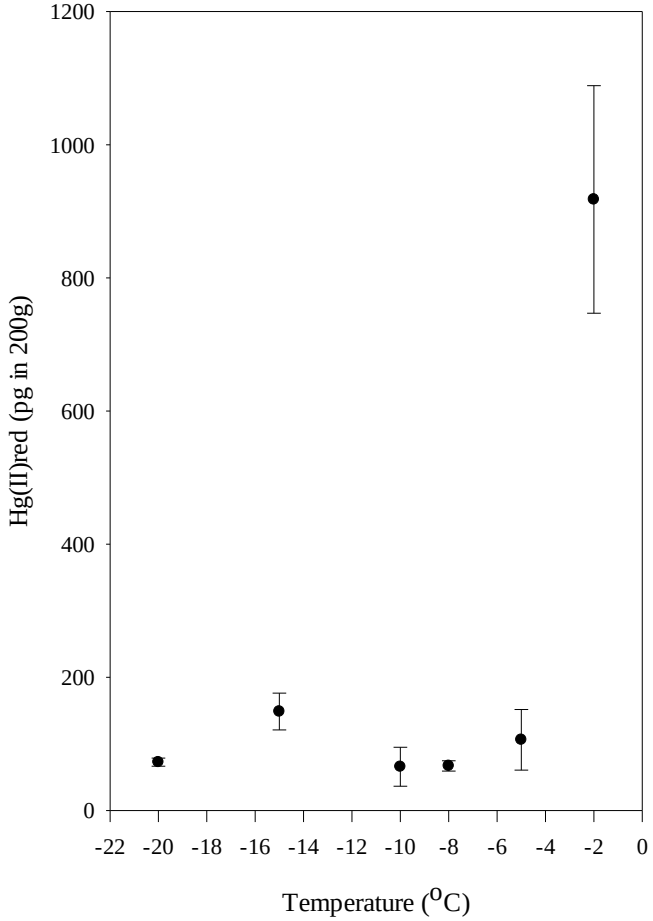

Figure 4.2: Total photoreduced mercury amounts for the 6 temperature trials, where the temperature given is the ambient air temperature in the freezer where the photoreactor was held. Error bars show the standard deviation the three trials run at each freezer temperature.

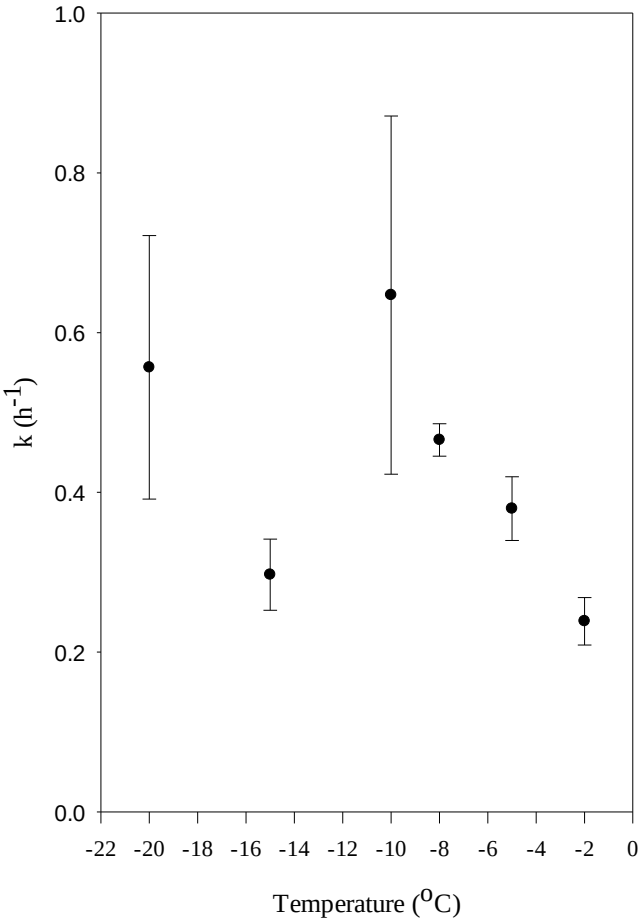

Figure 4.3: Pseudo-first order reduction rate constants for the 6 temperature trials, where the temperature given is the ambient air temperature in the freezer where the photoreactor was held. Error bars show the standard deviation the three trials run at each freezer temperature.

The presence of liquid in a snowpack has also been proposed to increase Hg reactions, leading to greater Hg(0) production (Faïn et al., 2007; Ferrari et al., 2005), and Dommergue et al. (2003) measured up to an order of magnitude increase in Hg reduction rate constants during the melt period, compared to pre-melt rate constants for a sub-arctic snowpack. However, freezing a liquid can also increase the rate of many reactions, including Hg reactions, because of the concentration of reactants into small liquid pockets within the frozen medium (O'Concubhair et al., 2012). We determined that the pseudo-first order Hg photoreduction rate constant decreased (slower rate of reduction) when

approaching the melting point, which may be due to the transition from QLL reactions in the frozen state to bulk liquid Hg(II) photoreduction reactions when the snow melts completely. In addition Ferrari et al. (2008) determined that more snowpack Hg exists in "stable" or less photoreducible forms when snow is close to melting, suggesting that the smaller photoreduction rate constants determined for higher temperature are occurring as a result of the increase in the fraction of "stable" Hg species compared to lower-temperature snowpack "stable" Hg amounts.

Observationally, field data showed a statistically significant influence of temperature on the flux of Hg(0) from Arctic snow; however, we have concluded that while temperature is important, it does not appear to be the most important factor determining the flux of Hg(0) from snow. Cross correlation analysis implies that temperature did not directly alter the kinetics of Hg photoreactions in Arctic snow. We propose that temperature changes Hg reactant availability by altering the relative proportions of solid and liquid water in the snowpack. Experimentally we noted no significant temperature effects on the rate constant (k), or total photoreduced Hg amount ($Hg(II)_{red}$), until air temperatures approached -2 °C and snow melts. Above -5 °C we observed an order of magnitude increase in the amount of Hg being photoreduced in the sample, with an approximately two-fold decrease in the rate of that photoreduction (Figs. 4.2, 4.3). An indirect influence of temperature on Hg photoreduction in snow due to an alteration of the liquid: water ratio was supported by laboratory and field measurements. Despite the cold air temperatures observed during the field study, there were periods where the surface snow temperature increased above -5 °C (Fig. 4.1), which may have

resulted in a larger release of Hg(0) with photoreduction. As such, these periods with temperature above -5 °C could be driving the significant relationship observed between temperature and Hg(0) flux in the field data, as predicted by the GAM. However, our research was limited by a lack of fine temperature resolution between -5 – 0 °C, which appears to be a critical temperature range for Hg photoreaction kinetic changes in Arctic snow. Future research should concentrate on investigating this temperature range in greater detail in the lab, and obtaining high time resolution data in the field during the important frozen to melted snowpack transition period. Despite these limitations, our research does have implications for changing Arctic conditions. With increasing Arctic temperatures, especially during periods with snow cover, more instances of conditions in the -5 – 0 °C could occur, which could, in turn, alter the amount of Hg available for photoreduction and the photoreduction rate.

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CHAPTER 5: INCREASING CHLORIDE CONCENTRATION CAUSES RETENTION OF MERCURY IN ARCTIC SNOW DUE TO CHANGES IN PHOTOREDUCTION KINETICS

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Abstract:

Mercury (Hg) in the Arctic is a significant concern due to its bioaccumulative and neurotoxic properties, and the sensitivity of Arctic environments. Previous research has found high levels of chloride (Cl^-) coinciding with high snowpack Hg loads. We hypothesize that Cl^- increases Hg retention by decreasing Hg photoreduction in Arctic snow. Changes in Hg photoreduction kinetics in melted snow from Alert, NU, Canada, were quantified with changing Cl^- concentration and UV radiation intensity. To do this snow was collected (May 2014) and melted in Teflon bottles, spiked with 0 – 10 ppm Cl^-, then irradiated with 3.52 – 5.78 $W \cdot m^{-2}$ UV (280 – 400 nm) radiation. Chloride concentration and photoreduction rate constants (*k*) had a positive linear relationships (*k* = 0.14 – 0.59 h^{-1}, with increasing Cl^-), while photoreducible Hg amounts ($Hg(II)_{red}$) had negative linear relationships with Cl^- ($Hg(II)_{red}$ = 1287 – 64 pg in 200 g melted snow, with increasing Cl^-). Varying UV and Cl^- concentration both altered $Hg(II)_{red}$ amounts, with Cl^- stabilisation of Hg more efficient under higher UV conditions, while *k* was controlled primarily by Cl^- concentration when both UV and Cl^- varied. Overall, with the expected greater Cl^- loading to Arctic snow, more Hg could be retained to move to aquatic ecosystems, potentially exposing organisms to more Hg.

1 Introduction:

1.1 Mercury speciation and reactivity in the Arctic:

Mercury (Hg), a neurotoxic and bioaccumulative environmental contaminant, exists in three main environmentally relevant forms: elemental (Hg(0)), divalent (Hg(II)) and

methyl mercury (MeHg) (Schroeder and Munthe, 1998; Steffen et al., 2008). Hg(0) is the main form found in the atmosphere (Lindqvist and Rodhe, 1985; Morel et al., 1998; Wängberg et al., 2007), while Hg(II) exists in condensed phases, like water, soils and snow (Dommergue, 2003; Fain et al., 2006; Ferrari et al., 2004b; Moore and Castro, 2012; Obrist et al., 2014; Sigler and Lee, 2006). MeHg is the bioaccumulative and neurotoxic form of Hg, and as such is found in organisms (Lindberg et al., 2002; Morel et al., 1998), as well as condensed phases (Ramlal et al., 1993). Hg can move between these different species in the environment, thereby altering its environmental fate.

The Arctic is a Hg-sensitive region, where organisms have been found to accumulate high Hg loads (Carrie et al., 2010; Kirk et al., 2012; Muir et al., 1992). Snow is one way by which Hg enters the surface environment and once melted is a vector for Hg transport into aquatic ecosystems where organisms may be exposed (Dommergue et al., 2010; Loseto et al., 2004). Hg deposited to snow with wet and dry deposition can be very labile (Lalonde et al., 2002; Poissant et al., 2008; Schroeder and Munthe, 1998), and so the speciation and magnitude of Hg contamination in Arctic snow is not constant after deposition, but will change due to snowpack reactions. The primary mechanism for Hg loss from snow prior to the snow melt period is through photochemical reduction of Hg(II) to Hg(0) (Durnford and Dastoor, 2011; Lalonde et al., 2002b; Mann et al., 2014, 2015; Poulain et al., 2004). Since Hg(0) does not sorb appreciably to ice crystals (Bartels-Rausch et al., 2008; Ferrari et al., 2004a), photoproduced Hg(0) can move from the snowpack back to the atmosphere with chemical/temperature gradients (Albert and Shultz, 2002; Anderson and Neff, 2008; Kuhn, 2001) and through snowpack ventilation

(Ferrari et al., 2005). Alternatively, Hg(0) can be photooxidized back to Hg(II) and remain in the snowpack (Lalonde et al., 2003; Poulain et al., 2004).

As snow melts the contaminants contained within can be transported with meltwater. Ionic components, including Hg, leave primarily in the first fractions of the meltwater (Dommergue et al., 2010; Kuhn, 2001), effectively becoming concentrated in the aqueous phase during first days of the snow melt period (Dommergue et al., 2010). This meltwater can then sit over sea ice or move directly into lakes, wetlands and the Arctic Ocean, transporting the contained Hg into these ecosystems. Clearly, an accurate description of the photochemical dynamics of Hg reactions in snow is important for correctly describing and predicting Hg behaviour in Arctic environments. Interactions of Hg with ions are important, but presently are poorly quantified. In particular, chloride (Cl^-) is suspected to affect Hg photochemical reactions in Arctic snow, but the magnitude of the effect on Hg reaction kinetics has not been fully quantified (Mann et al., 2014, 2015).

1.2 Mercury and chloride interactions:

Elevated Cl^- concentrations have been found to co-exist with high Hg levels in Arctic snow, which has led to the thought that Cl^- may help retain Hg in these environments. Several groups have measured increasing Hg in Arctic snow with decreasing distance from oceanic coasts, or leads/polynyas (Constant et al., 2007; Douglas et al., 2005; Garbarino et al., 2002). Douglas et al. (2005) quantified Hg in frost flowers near Barrow, Alaska, which are known to have high Cl^- concentrations (salinity =

60-120 psu), and found up to 820 ng/L Hg, with Hg concentrations increasing as the frost flowers aged due to Hg(0) scavenging, as well as higher Hg concentrations in snow near open water compared to snow further inland. Sherman et al. (2012) also found elevated and increasing Hg concentrations in frost flowers as they aged, which they proposed was due to scavenging of gas phase Hg by the high Cl^- frost flowers. Poulain et al. (2007a) found significantly higher Hg concentrations in snow over sea ice compared to inland snow. The high Hg concentrations observed have been proposed to be caused by Cl^- in one of two ways: either by enhancing the photooxidation of Hg, thereby decreasing loss of Hg(0) from snow and/or scavenging Hg(0) from the atmosphere, or by decreasing the extent of photochemical reduction of Hg(II) through the formation of stable Hg chlorocomplexes. Lalonde et al. (2003) observed Hg(0) oxidation in temperate snow samples spiked with Cl^- from the Experimental Lakes area in Ontario, Canada, and concluded that snow with more Cl^- produced less Hg(0) by favouring photooxidation of Hg(0) over photoreduction of Hg(II). Amyot et al. (2003) concluded that the presence of Cl^- in Arctic snow favours photooxidation over photoreduction, stating that Hg in Arctic inland snow would be more susceptible to re-release with photoreactions than that near the coast. Steffen et al. (2013) observed decreased GEM emissions from snow over sea ice, compared to inland snow in the Arctic, which was attributed to the higher Cl^- concentration in the snow over sea ice. Further, Steffen et al. (2013) concluded that snow over sea ice will retain significantly higher amounts of Hg than overland snow, and this needs to be included in future modelling pursuits, as it is presently ignored. In their laboratory study, Bartels-Rausch et al. (2011) observed a decline in photolytically produced Hg(0) in thin ice films with higher Cl^- concentrations. St. Louis et al. (2007)

observed a significant positive correlation between Cl^- and Hg concentrations in Arctic snowpacks, and proposed the formation of stable Hg chlorocomplexes as the cause. Poulain et al. (2007a) determined that more Hg binds to particulates in snow with higher Cl^- concentrations, thereby leading to less Hg photoreduction, since particle bound Hg is generally not considered to be photoreducible (Brooks et al., 2006).

While many studies have identified the potential importance of Cl^- to Hg photoreduction, a critical analysis of the relationship between Cl^- concentration and Hg photoreduction kinetics has not yet been undertaken. This research aims to quantify the effect of Cl^- concentration on the kinetics of photochemical reduction of Hg in melted Arctic snow in a controlled setting, thus reducing the variability due to *in situ* differences in Cl^- concentrations and changing natural environmental conditions. We hypothesize that increasing Cl^- concentrations would result in greater retention of Hg in melted Arctic snow, and that the kinetics of Hg photoreduction would be affected. To test this, chloride was added to melted snow and samples were irradiated with a constant intensity of UV radiation (3.52 – 5.78 $W \cdot m^{-2}$) at constant temperature (4 °C) in a controlled laboratory setting. From this work the rate constant (k) and total amount of photoreduced Hg ($Hg(II)_{red}$) were determined for various concentrations of added Cl^- (0 – 10 ppm added Cl^-), and relationships between kinetic (k and $Hg(II)_{red}$) and environmental (UV intensity and Cl^- concentration) variables were derived.

2 Methods

2.1 Sample collection:

Surface snow (<15 cm) was collected at the Environment Canada Alert NU observatory (82°28'N, 62°30'W) on 11-13 May, 2014. Snow was scooped into 2.2L Teflon (PTFE) bottles using an acid-washed plastic trowel and then melted at room temperature in the dark. Melted snow samples were pooled and re-frozen in 2.2L bottles for storage and transport to Acadia University for analysis.

2.2 Sample analysis:

To determine the influence of chloride (Cl^-) on the kinetics of Hg photoreduction, 0 – 10 ppm Cl^- (as sodium chloride) was added to melted samples in 2.2L bottles. Individual aliquots were frozen in 50 mL HDPE conical vials and stored in the dark at -20 °C. Two vials were removed to thaw completely, in the dark, on the day of analysis.

The kinetics of Hg photoreduction were determined using the method described by Mann et al. (2015) for melted snow, as well as O'Driscoll et al. (2006) and Qureshi et al. (2010) for freshwater and ocean water samples, respectively. Briefly, 90 – 100 mL of melted sample was poured into an acid washed pre-irradiated quartz beaker and weighed. Samples were bubbled with Hg-free zero air (Tekran 1100) in the dark to remove existing Hg(0). Blanked samples were then irradiated with constant UV radiation (280 – 400 nm) from 3.52 to 5.78 $W \cdot m^{-2}$ in a LuzChem photoreactor. All instruments were placed in a walk-in refrigerator at 4±1 °C. Evolved Hg(0) was continuously flushed from samples with Hg-free zero air bubbled through the water column, and quantified with a Tekran 2537A cold vapor atomic fluorescence spectrometer. Irradiation of samples continued until the Hg(0) concentration fell below the detection limit (0.1 $ng \cdot m^{-3}$) for at least 1 h.

Pseudo-first order photoreduction rate constants (*k*) and photoreduced Hg amounts ($Hg(II)_{red}$) were determined using curve fitting in SigmaPlot 12 (Equation 5.1). Photoreduced Hg amounts were mass corrected to 200g to account for sample mass variability between trials.

$$Hg(0) = Hg(II)_{red} \cdot (1 - e^{-k \cdot t}) \quad \text{(Equation 5.1)}$$

Samples were analysed for total Hg (THg) concentrations (both post-irradiation and non-irradiated samples). THg was determined using a Tekran 2600 Total Hg analyser for aqueous samples and following the US EPA's Method 1631 (US EPA, 2002), where unfiltered samples were preserved with bromine monochloride addition (0.25%), and THg quantified with stannous chloride reduction and cold vapour atomic fluorescence detection.

3 Results and Discussion:

3.1 Photoreduced Hg amounts:

Photoreduced Hg amounts ($Hg(II)_{red}$), or amounts of Hg(II) reduced to Hg(0) and liberated from the sample with exposure to UV radiation, were plotted against added Cl^- concentration, with data grouped by UV intensity (Fig. 5.1). $Hg(II)_{red}$ values decreased with increasing added Cl^- concentration for all UV intensities. This means that increasing Cl^- caused less of the Hg in melted snow to be photoreducible under the experimental conditions. A plot of the slopes of $Hg(II)_{red}$ vs. added Cl^- concentration against UV intensity (Fig. 5.2) showed a negative linear relationship ($R^2 = 0.85$, $p < 0.05$), where the slope of $Hg(II)_{red}$ vs. added Cl^- concentration describes the efficiency or rate of Hg

stabilisation by Cl^- in the melted snow. These results suggest that Cl^- has a greater stabilisation effect (larger negative value for slope of $Hg(II)_{red}$ vs. Cl^-) at higher UV intensities compared to low UV intensities. As such, in high Cl^- environments, UV intensity may be less important than Cl^- concentration for determining how much Hg can be photoreduced in melted snow, due to this Cl^- stabilisation of Hg.

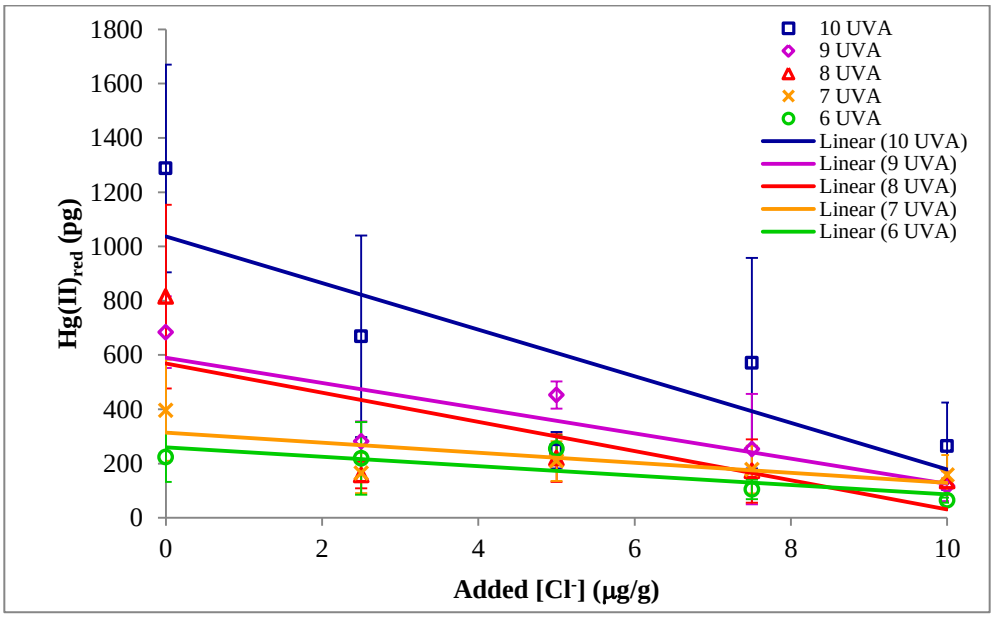

Figure 5.1: Photoreduced Hg amounts, grouped by incident UV intensity where 10 UVA = 5.78 $W \cdot m^{-2}$ (R^2 = 0.53; p = 0.1), 9 UVA = 5.22 $W \cdot m^{-2}$ (R^2 = 0.61; p = 0.07), 8 UVA = 4.65 $W \cdot m^{-2}$ (R^2 = 0.39; p = 0.1), 7 UVA = 4.09 $W \cdot m^{-2}$ (R^2 = 0.39; p = 0.1), 6 UVA = 3.52 $W \cdot m^{-2}$ (R^2 = 0.57; p = 0.08), for increasing chloride concentration.

Photoreduced Hg amounts decrease with increasing Cl^- concentrations in melted snow for all studied UV regimes. This supports the idea that increasing Cl^- stabilises Hg in the snowpack, perhaps through formation of stable Hg chloro-complexes as was proposed by St. Louis et al. (2007). It should be noted that there is the possibility that fast Hg(0) photooxidation occurred along with photoreduction in the beaker, which may have added some error to Hg(II) photoreduction measurements, since the Hg photoreduction rate and extent were determined based on the evolution and quantification of Hg(0) in

samples. However, this error should be minimal since the rate of removal of Hg(0) from the aqueous sample exceeds published Hg(0) photooxidation rates (Mann et al., 2015). As such, the observed decrease in $Hg(II)_{red}$ values were primarily the result of Hg(II) stabilisation, or decreased Hg(II) photoreduction. Hg(0) photooxidation in snow may be induced by Cl^- (Lalonde et al., 2003), which might suggest even higher levels of chloride mediated retention of Hg in *in situ* snow where both photooxidation and photoreduction occur coincidently. Therefore, the $Hg(II)_{red}$ values determined in this study represent the maximum amount of Hg(II) in melted snow that can be removed by photochemical means, since photooxidation is supressed. It should be noted that these conclusions are based on the study of melted snow samples, and as such, there may be differences in the absolute magnitude of effects observed in frozen snow, since Hg photoreduction kinetics can vary in frozen vs. melted snow samples (Mann et al., 2015). However, the relative relationships observed as a result of changing the chemical compostion of the snow should still hold true, and as such this work provides a valuable first approximation of the effects of Cl^- on Hg photoreduction in snow. In addition, the calculated efficiency of stabilisation of Hg(II) by chloride in the melted snow samples (Fig. 5.2) represents the minimum Cl^- stabilisation effect (CSE), and is a conservative quantitative measurement describing the influence of Cl^- concentration on the amount of Hg(II) that can be removed, by photochemical means, from melted Arctic snow. This new measurement technique should prove useful in future as a quantitative indicator to compare the minimum CSE of Hg in aqueous samples between ecosystems.

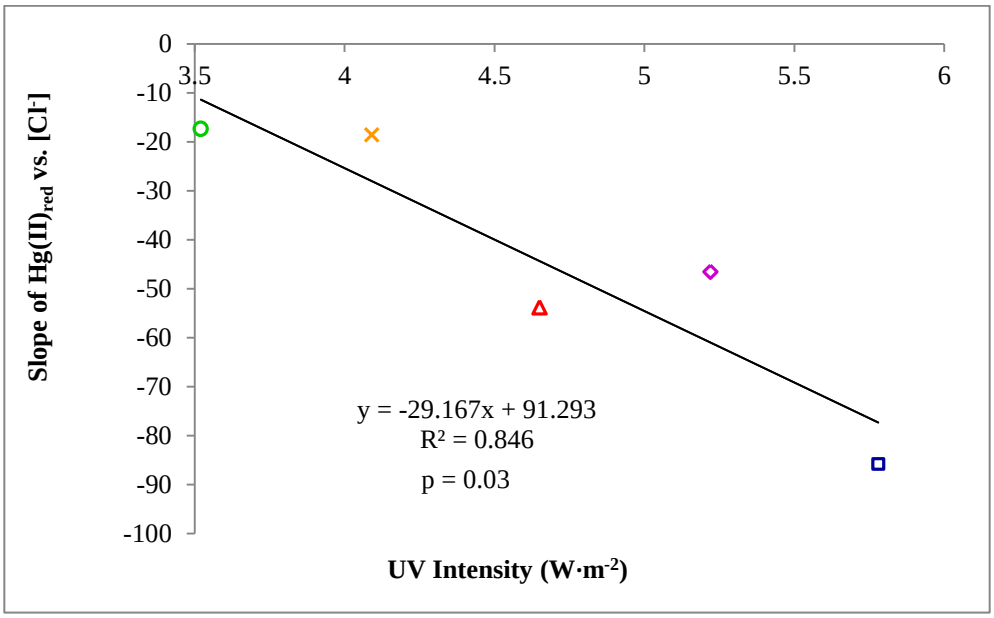

Figure 5.2: Slopes of photoreduced Hg amounts vs. added chloride concentration lines, or Cl^- stabilisation effect (CSE), (Fig. 5.1) plotted against incident UV radiation intensity.

3.2 Total Hg in irradiated samples

Total Hg in melted snow samples was 39.4 ± 10.7 ppt (n = 15) prior to irradiation and did not significantly change post irradiation (t-test: $p > 0.05$). While this may appear counter-intuitive, appreciable Hg was lost from samples with irradiation (0.8 – 16 %). Since irradiated samples were unfiltered, some additional Hg may have been solubilized from particles following BrCl addition. Particle bound Hg is not thought to be photoreducible (Durnford and Dastoor, 2011), and so would not have been subject to photochemical reaction during the irradiation experiments. In addition, it can be seen that the standard deviation of the THg concentration in the non-irradiated snow from Alert was quite high, which may mean that a small change in THg with irradiation is masked by the large variability in THg between trials. The large standard deviation on the non-irradiated melted snow THg concentration may be due to small differences in the

concentration of particles in different samples, or slight variation in the size/Hg concentration of the particles, since we are considering trace-level THg concentrations. However, neither of these potential differences in particles contained between replicates would influence photoreducible Hg amounts to a great degree, since particle bound Hg is not generally thought to be photoreducible.

3.3 Pseudo-first order photoreduction rate constants:

Hg photoreduction is faster at greater Cl^- concentrations, since pseudo-first order photoreduction rate constants (*k*) increase with increasing added Cl^- concentration for all UV irradiation intensities (Fig. 5.3). Plotting the slopes of *k* vs. added Cl^- concentration against the incident UV radiation intensity showed no significant trend (Fig. 5.4). These results suggest that the influence of Cl^- concentration on the Hg photoreduction rate constant is the same for all intensities of incident UV radiation. As such, if both UV intensity and Cl^- concentration are varying in an environment, Cl^- concentration may be more important for determining *k* in melted Arctic snow. Since there was no significant difference in *k* for different UV intensities, the data can be combined to generate one plot and equation describing the influence of Cl^- concentration on *k* (Fig. 5.5). The equation from Fig. 5.5 is then suitable to predict pseudo-first order rate constants for Hg photoreduction in melted Arctic snow, knowing the Cl^- content in that snow, regardless of incident solar radiation.

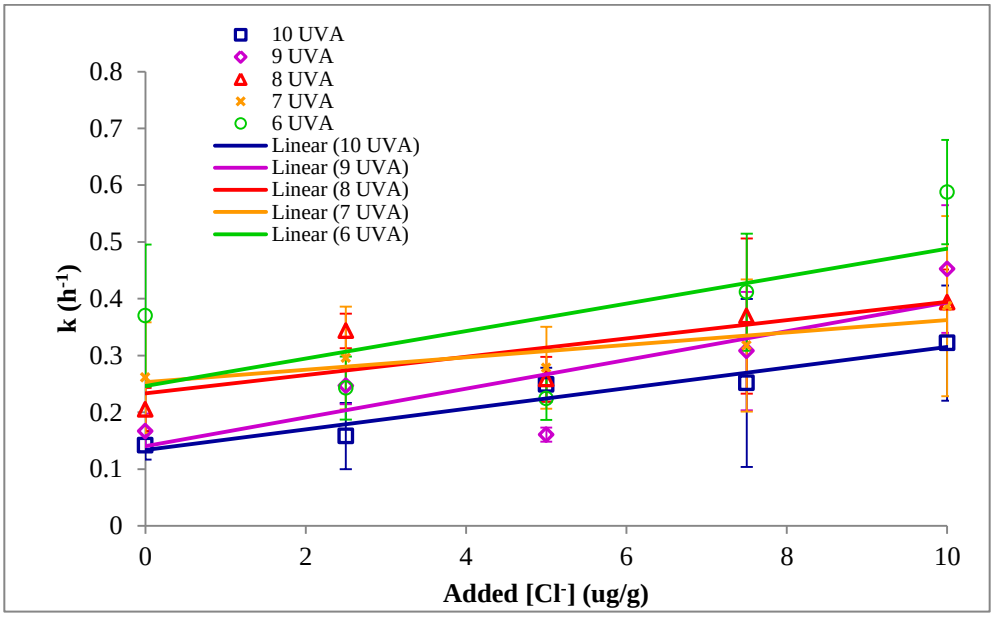

Figure 5.3: Pseudo-first order photoreduction rate constants, grouped by incident UV intensity where 10 UVA = 5.78 W·m^{-2} (R^2 = 0.91; p = 0.01), 9 UVA = 5.22 W·m^{-2} (R^2 = 0.59; p = 0.08), 8 UVA = 4.65 W·m^{-2} (R^2 = 0.52; p = 0.1), 7 UVA = 4.09 W·m^{-2} (R^2 = 0.71; p = 0.04), 6 UVA = 3.52 W·m^{-2} (R^2 = 0.23; p = 0.2), for increasing chloride concentration.

This equation can predict Hg photoreduction in Arctic snow based on pseudo-first order kinetics, and the Cl^- concentration of the snow in ppm (Equation 5.2). Previous research has named UV radiation as one, if not the most important factor in determining Hg photoreduction kinetics in Arctic snow (Durnford and Dastoor, 2011), and our present work did find that UV intensity has a significant influence on the rate of Hg photoreduction in melted snow. However, it was determined that in environments where both Cl^- concentration and UV radiation were changing, it is the Cl^- concentration that appears to be controlling the magnitude of the Hg photoreduction rate constant in melted Arctic snow, in the range of UV radiation studied (3.52 – 5.78 W·m^{-2}). This has important implications for modelling future Arctic Hg behaviour with changing climate conditions, especially considering that data existing in the literature has not allowed the inclusion of Cl^- dependence in Hg fate modelling (Steffen et al., 2013).

$$Hg(0) = Hg(II)_{red} \cdot \left(1 - e^{-(0.02[Cl]+0.2)\cdot t}\right)$$ (Equation 5.2)

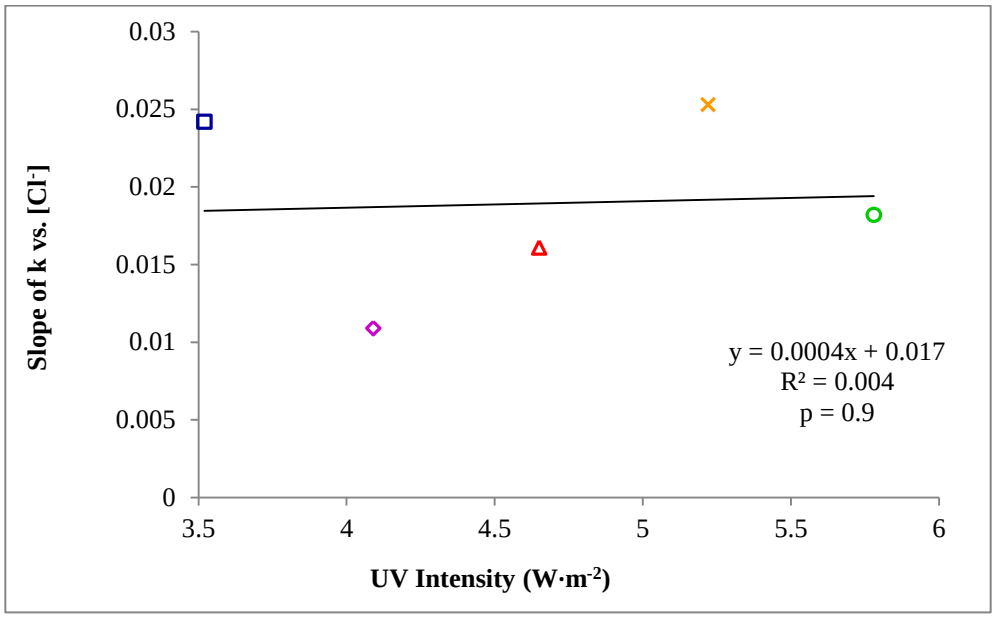

Figure 5.4: Slopes of pseudo-first order photoreduction rate constant vs. added chloride concentration lines (Fig. 5.3) plotted against incident UV radiation intensity.

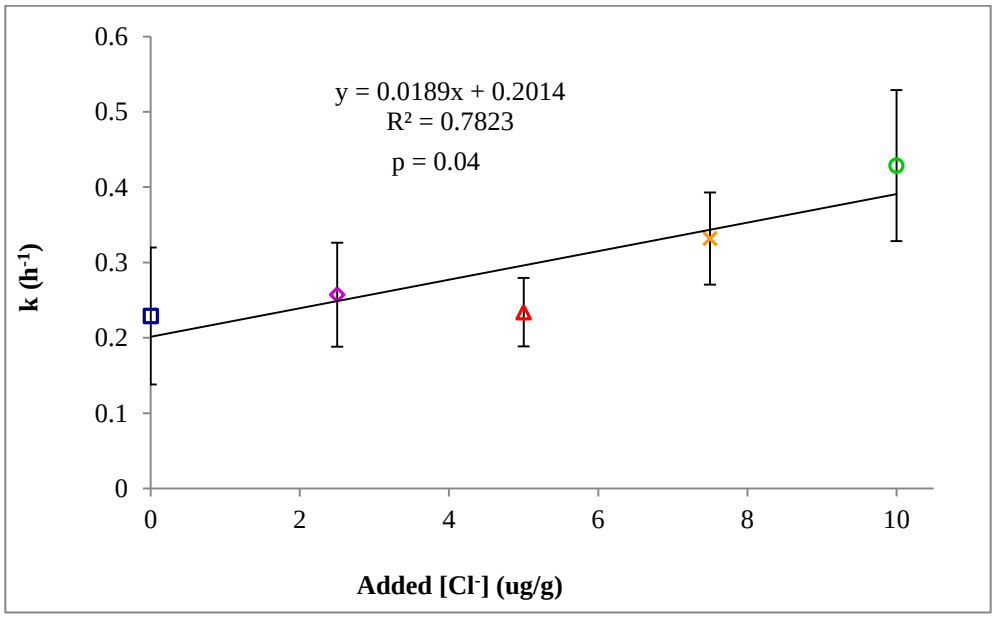

Figure 5.5: Pseudo-first order photoreduction rate constants for added chloride concentration. Data shown are the average for all 5 UV irradiation intensities (3.52 – 5.78 W m^{-2}) at a particular added chloride concentration, with error bars showing the standard deviation of the data.

Dommergue et al. (2007) reported values of 0.25 or 0.18 h^{-1} for Hg photoreduction rate constants, determined by monitoring the flux of Hg(0) from temperate, alpine and polar snow in a laboratory-based flux chamber. Mann et al. (2015) found Hg photoreduction rate constants of 0.11 – 0.60 h^{-1} in frozen Arctic snow irradiated in the laboratory with varying intensities of UV radiation. Others have reported Hg photoreduction or Hg(0) photoproduction rates of 1.33 $pmol \cdot L^{-1} \cdot h^{-1}$ in Arctic snow irradiated *in situ* (Poulain et al., 2004), 0.04 $pmol \cdot L^{-1} \cdot h^{-1}$ and 0.27 $pmol \cdot L^{-1} \cdot h^{-1}$ for temperate snow irradiated under canopy cover and open sky, respectively (Poulain et al., 2007b), or 1.6 $pmol \cdot L^{-1} \cdot h^{-1}$ for temperate snow irradiated *in situ* (Lalonde et al., 2002). Few studies have explicitly measured Hg photoreduction rate constants in melted snow; however, Mann et al. (2015) determined rate constants from 0.08 – 1.05 h^{-1} for melted Arctic snow subject to different intensities of UV radiation in the lab. Dommergue et al. (2003) found the rate of Hg(0) production in a sub-Arctic snowpack at the onset of melt to be an order of magnitude higher than that prior to the melt period (0.006 – 0.02 $pmol \cdot L^{-1} \cdot h^{-1}$ and 0.0006 – 0.02 $pmol \cdot L^{-1} \cdot h^{-1}$, respectively). Rate constants determined here (0.14 – 0.59 h^{-1}) for melted snow from Alert with varying Cl^- concentration and UV irradiation intensity are consistent with other published values, and cover a large fraction of the reported variability in Hg photoreduction rate constants in frozen/melted snow. It is very likely that some of the variability seen in published Hg photoreduction rates and rate constants is due to variability in snowpack Cl^- concentrations, lending more evidence to the idea that inclusion of Cl^- dependence in the description of Hg cycling and fate is critical for the better prediction of Hg environmental behaviour.

The greater *k*-values measured with increasing Cl^- concentration mean faster photoreduction of Hg as Cl^- increases. Since the method used to quantify Hg photoreduction separates photoreduction and photooxidation by removing Hg(0) as it forms (Mann et al., 2015), these *k*-values do not necessarily describe the net photoreduction rate or flux of Hg(0) from snow that will be measured *in situ*, since photooxidation and photoreduction occur together in the field. However, the determined *k* values can be thought of as the maximum rate of removal of Hg(II) from melted Arctic snow by photochemical means, providing an upper boundary or a greatest potential loss of Hg under the influence of varying Cl^- concentration.

3.4 Implications for the Arctic

Changing climate conditions are resulting in the potential for greater accumulation of Cl^- in Arctic snow. With the observed and future predicted tendency towards thinner, saltier sea ice, with a shorter ice covered period and more open water (Comiso, 2006; Kattsov et al., 2005; Meier et al., 2007; Rothrock et al., 1999), more sea salt aerosol can deposit NaCl to the nearby surface snow and unfractionated sea salt is the primary source of many ions, including Cl^- to coastal snow (Krnavek et al., 2012). The presence of more Cl^- in snow can result in greater accumulation or retention of Hg in Arctic snow (Garbarino et al., 2002; Larose et al., 2010; Poulain et al., 2007b, 2004; Steffen et al., 2013; St. Louis et al., 2007). In this work, higher Cl^- concentrations resulted in less Hg photoreduction which supports the hypothesis that Cl^- stabilises existing Hg(II), possibly through formation of stable Hg chlorocomplexes, as proposed by St. Louis et al. (2007).

The formation of these chlorocomplexes would mean that less of the Hg is available for photoreduction, leading to a greater overall movement of Hg into receiving water bodies in the spring with snow melt. The presence of more Hg in the melt water may result in increasing Hg contamination of foodwebs, as, more Hg could move into organisms, exacerbating the existing Arctic Hg problem for humans and other organisms who live in or seasonally visit the region to feed and breed.

The quantitative predictive equations provided here for Hg photoreduction rate constants, photoreduced Hg amounts, and measurements of the chloride stabilization effect, can be included in future Hg cycling models or predictive Hg fate and transfer models. Snow over sea ice has been proposed to be particularly poorly modelled (Steffen et al., 2013), since the relationships between Hg photoreactions and Cl^- load had not been determined. With the relationships elucidated in this work we can now better predict Hg retention in snow and Hg photoreduction kinetics, knowing that Cl^- concentration is a key factor.

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CHAPTER 6: SUMMARY

1 General Conclusions

Hg photoreactions in snow are very dynamic and have been shown to be influenced by many different environmental factors. Laboratory experiments in 2012, chapter three of this thesis, investigated the influence of UV radiation intensity on Hg photoreaction kinetics in frozen and melted Arctic snow. We determined that photoreducible Hg amounts increased linearly with increasing UV intensity, while rate constants displayed a parabolic relationship, with highest rate constants found for low and high UV irradiation intensities. In addition, differences in the kinetics of Hg photoreactions were found in snow from the three sites collected in March in Resolute Bay, NU, which was proposed to be due to differences in snowpack chemistry.

From *in situ* Hg(0) field flux measurements in Resolute Bay, NU in March 2013, chapter four of this thesis, we determined that snow age, or time since snow fall, and snow temperature both had statistically significant influences on Hg(0) flux from Arctic snow, though it was likely that neither of these factors is most important in determining Hg(0) flux from snow. Cross correlation analysis of the 2013 field Hg(0) flux data revealed a 30 min time lag between changes in snowpack temperature and changes in Hg(0) flux from snow. This indicates that temperature did not cause immediate changes in Hg(0) flux, and so was likely not directly influencing Hg photoreduction kinetics in Arctic snow by influencing the energetics of the reactions. In contrast, Hg(0) flux from snow lagged UV radiation intensity changes by only 5 min, which means that a change in

UV radiation intensity caused a near immediate change in Hg(0) flux. These results imply that Hg photoreduction kinetics were directly influenced by UV radiation intensity. From controlled laboratory work in 2013 investigating the -2 to -20 °C temperature range, with Arctic snow exposed to constant intensity UV irradiation, temperature did not have a significant effect on Hg photoreduction kinetics until snow approached the melting point. When snow began to melt, photoreduced Hg amounts increased and photoreduction rate constants decreased.

Laboratory investigations in 2014, chapter five of the thesis, varied chloride concentrations in snow collected from Alert, NU in May 2014, through the controlled addition of sodium chloride to melted Arctic snow. Melted snow was irradiated at constant temperature (4 °C) to determine the kinetics of Hg photoredution with varying chloride concentration and UV radiation intensity. From these experiments, we determined that both chloride and UV radiation intensity influence Hg photoreduction rate constants and photoreducible Hg amounts in melted snow. Higher chloride concentrations resulted in lower photoreducible Hg amounts, but higher Hg photoreduction rate constants. However, when both chloride concentration and UV intensity varied simultaneously, chloride concentration mainly controlled the Hg photoreduction rate constant, since all UV irradiations experienced similar increases in the Hg photoreduction rate constant with increased added chloride.

2 Specific applications

With the kinetic data derived in this thesis work, it will be possible for future researchers to better model photoreduced Hg amounts and Hg photoreduction rate constants in Arctic snow having some limited site-specific data (i.e. chloride concentration and/or the UV radiation intensity received at the site). Such estimates for Hg photoreaction kinetics in Arctic locations have previously been lacking in the literature and the effects of climate change on these parameters are highly uncertain. Temperatures are expected to increase in Arctic locations, making the onset of snowmelt earlier and thereby exposing frozen and melted snow to differing (lower) UV radiation intensities. In addition, Arctic Ocean sea ice cover will continue to decrease, which could result in higher chloride loading to the surrounding coastal snow, or snow over remaining sea ice. The relationships derived in this thesis between Hg photoreaction kinetics and these changing environmental variables will allow researchers to predict the influence of Arctic climate change on Hg fate. This is a critical gap for cryospheric Hg modelling efforts in the Arctic and global environments.

Models such as the Global/Regional Heavy Metals Model (GRAHM) and GEOS-Chem will benefit from the results presented in this thesis. The relationships presented here can be used to provide much needed Hg emissions from snow, improving the general Hg emissions budget, since Hg re-emission values tend to be very uncertain, or simply ignored (AMAP, 2011; Kirk et al., 2012). The availability of rate constants will also allow for the removal of some simplifying assumptions in current Hg models. Models such as the ones used by Diamond (1999), Toose and Mackay (2004), MacLeod et al. (2005) and Ethier et al. (2008) implicitly deal with changes in Hg speciation due to

reaction by assuming or calculating Hg species ratios or fractions within an environmental compartment. It should be noted that the ratio method makes many general assumptions, including that Hg fate can be predicted based on Hg(0) movements, in a fashion similar to less reactive environmental contaminants, which is an assumption that may not be valid for the very environmentally reactive Hg. However, with Hg photoreduction and photooxidation rate constants, actual rates of Hg conversion between oxidized (Hg(II)) and reduced (Hg(0)) forms can be calculated, improving the predictive power and accuracy of these models (Toose and Mackay, 2004). Models, such as the one described by Carroll et al. (2000) explicitly deal with Hg species interconversion by requiring input of Hg reaction rates, while Durnford et al. (2012) added dynamic Hg deposition and re-emission to GRAHM. These models would also benefit from the Hg kinetic relationships derived in this thesis, since Hg photoreduction rates relative to environmental parameters would allow modelling of Arctic Hg cycling in environments where these reaction rates have not been explicitly measured, but UV intensity and/or chloride concentrations are known, or can be predicted based on known or future predicted climate values.

3 Future work

The work described in this thesis provides valuable information, furthering our understanding of Hg dynamics in Arctic environments, and potentially increasing the predictive power of existing Hg fate and transport models by defining novel equations and relationships that can be used to determine Hg photoreduction rate constants.

However, there are still many more studies building on the information provided here that would be valuable for furthering our understanding of global Hg cycling and Arctic cryospheric Hg dynamics. A logical next step would be to incorporate the kinetic relationships into several current Hg models, where Hg photoreduction is predicted based on chloride concentration and/or UV radiation intensities received by the snowpack. From such a model, Hg(0) flux from snow could be predicted. These modelling results could then be validated against flux values like those presented in chapter four. In addition, further Arctic snowpack Hg(0) flux measurement should be undertaken at a range of Arctic sites and chloride concentrations measured in addition to UV radiation intensities.

Other steps forward from this thesis work would be to further increase the range of chemicals studied for Hg photoreaction dependence. It was postulated in chapter three that iron may influence Hg photoreduction rates in Arctic frozen/melted snow, as iron has been found to affect Hg photoreduction dynamics in other aqueous media (Zhang and Lindberg, 2001); however, this was not pursued in subsequent studies here. In addition, bromine is particularly important to atmospheric Hg photoreactions (Ariya et al., 2002; Holmes et al., 2009), and so could potentially influence Hg photoreactions in snow as well.

It would be extremely valuable to increase the knowledge around chloride dependence of Hg photochemical reactions. In melted snow (chapter five) chloride concentration was more important than UV intensity in determining Hg photoreduction rate constants, when both were varied; however, it was not possible in these studies to

examine the influence of chloride on frozen snow, since the methods used did not allow spiking of frozen snow samples with chloride. To examine the influence of chloride on Hg photoreduction kinetics in frozen snow, it would be very useful to have access to Arctic snow with a natural range of chloride concentrations (inland, coastal, over sea ice). This experimental design would allow for the determination of these relationships for frozen snow. It is possible that the effects of chloride on frozen snow Hg photoreduction kinetics may differ slightly from those determined for melted snow, as was seen in chapter three when comparing Hg kinetics in frozen and melted snow.

In general, we were not able to explicitly study Hg photooxidation reactions in any great detail, and increasing knowledge of photooxidation kinetics and the dependence on environmental parameters would be extremely useful and a good extension of the data collected for this thesis. For example, it has been proposed that chloride influences Hg photoreaction dynamics by making photooxidation favoured over photoreduction (Amyot et al., 2003). However, with the experimental set up described in chapter five, we limited Hg(0) photooxidation by removing Hg(0) as it forms, and so no information on this proposed influence of chloride on Hg photooxidation was derived. A logical extension of the experiments undertaken would be to study the influence of chloride on Hg photooxidation in Arctic snow.

In undertaking the experiments described in this thesis, it became apparent that, to the best of our knowledge, there is no measurement of total UV intensity in Arctic locations with a sufficiently small time resolution to be useful for predicting Hg(0) photoreduction. Since it was determined that UV radiation intensity strongly affects Hg

photoreaction kinetics in Arctic snow (chapters 3 and 5), it would be very useful, for modelling pursuits, to have at least one full year of hourly Arctic UV intensities at a range of latitudes. During the March 2012 and 2013 field campaigns, UV intensities were measured; however, aside from these data we were unable to locate UV intensities for other times of the year (spring into summer). This means we do not know whether we have covered the full range of UV intensities possible during the season where snow exists and subsequently melts, though it is likely we have not, based on the UV intensity results collected during the *in situ* field study (Chapter 4). With better knowledge of the possible intensities, the range of UV intensities for which Hg photoreaction kinetics are quantified could be increased, thereby reducing the potential error that may be associated with using the derived equations outside the UV study range and increasing the predictive power of the equations and models making use of them.

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APPENDICES

Appendix 1: Chapter 3: Mercury in Arctic snow – Quantifying the kinetics of photochemical oxidation and reduction

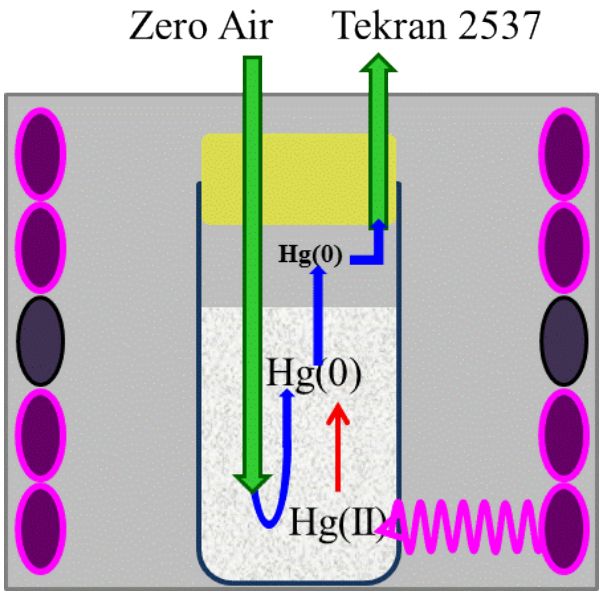

Figure A1.1: Schematic showing the experimental set up for Hg photoreduction kinetic determination. Acid washed pre-irradiated quartz beakers are filled with snow and irradiated in a LuzChem photoreactor while Hg(0) is quantified through time (Tekran 2537) to determine the kinetics of Hg photoreduction. Frozen samples are maintained at -10 °C and melted samples at 4 °C.

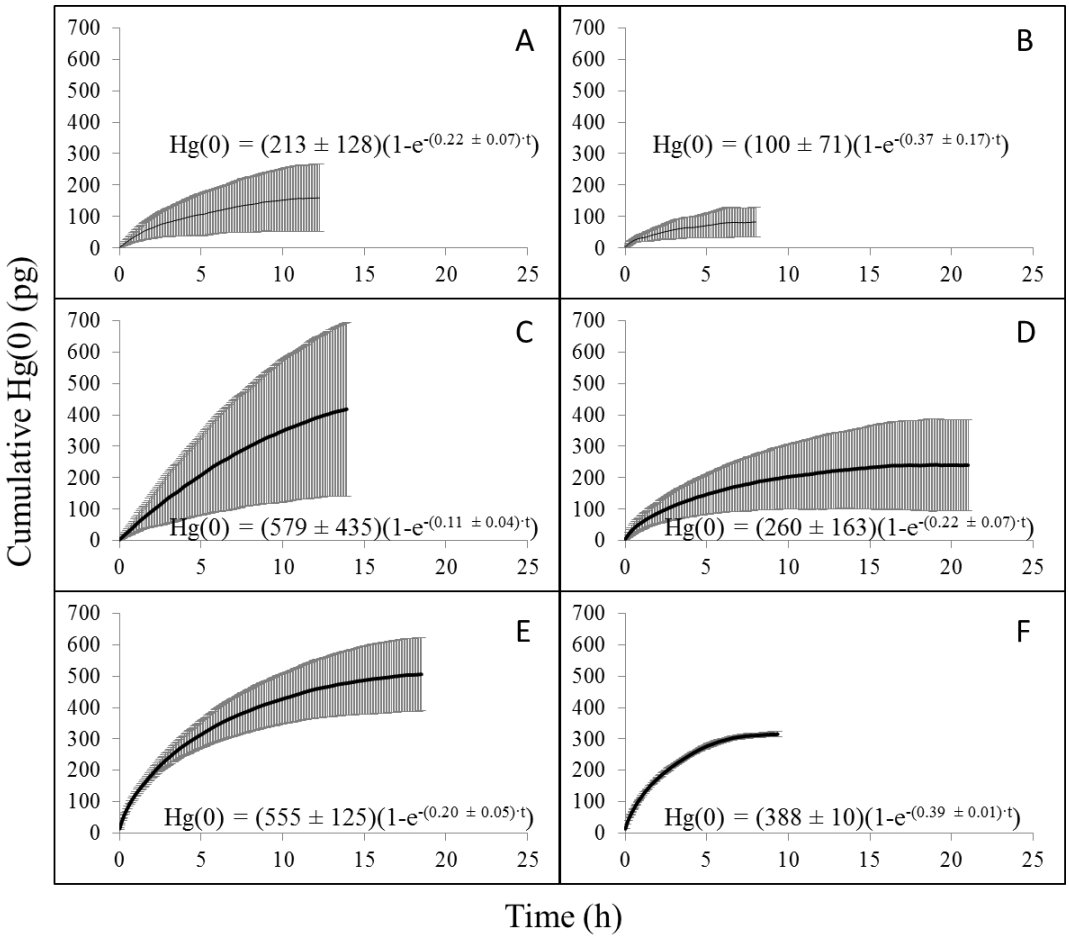

Figure A1.2: Site 1 cumulative Hg(0) collected over the irradiation period for 1.26 $W \cdot m^{-2}$ (A), 1.83 $W \cdot m^{-2}$ (B), 2.39 $W \cdot m^{-2}$ (C), 3.52 $W \cdot m^{-2}$ (D), 4.65 $W \cdot m^{-2}$ (E), and 5.78 $W \cdot m^{-2}$ (F) of UV (280 – 400 nm) radiation with the associated Equation 3.1 for each intensity. Average Hg(0) for three trials is shown as a black line, while error bars (± standard deviation) are shown in grey.

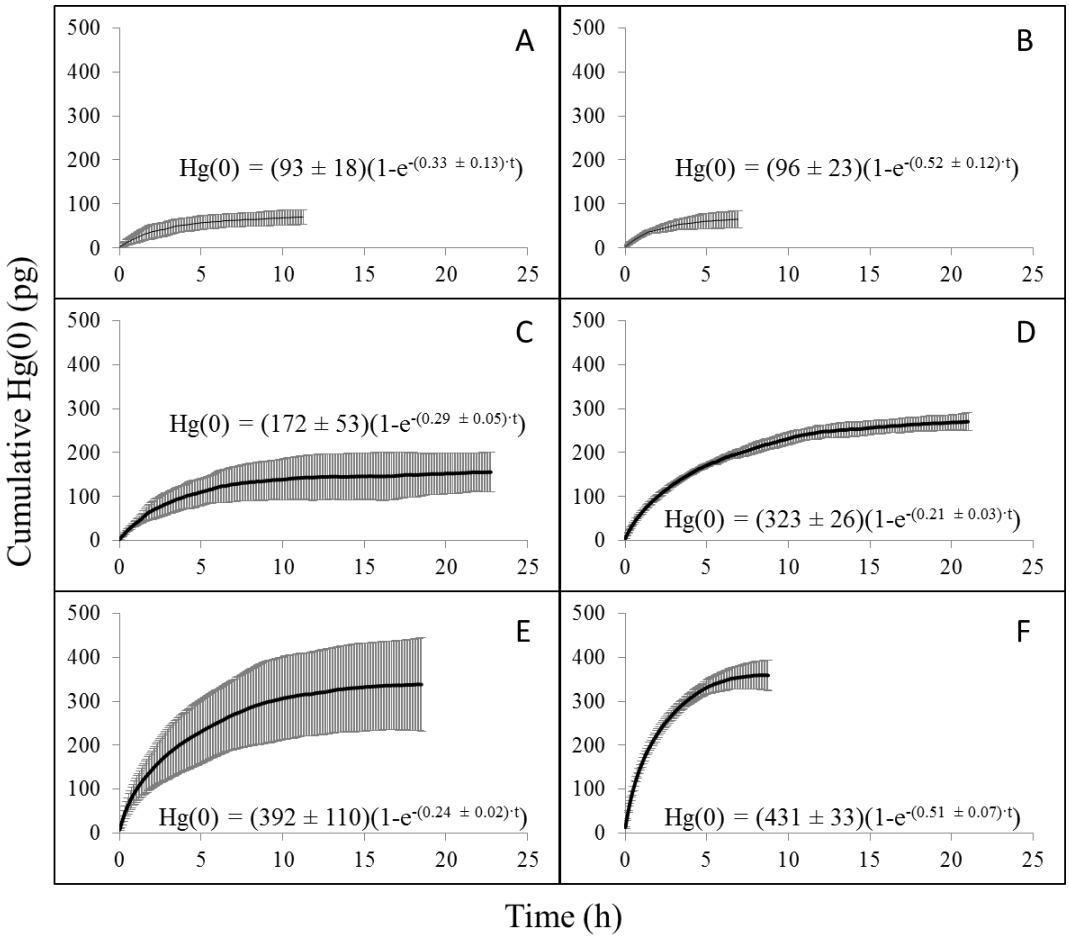

Figure A1.3: Site 2 cumulative Hg(0) collected over the irradiation period for 1.26 $W \cdot m^{-2}$ (A), 1.83 $W \cdot m^{-2}$ (B), 2.39 $W \cdot m^{-2}$ (C), 3.52 $W \cdot m^{-2}$ (D), 4.65 $W \cdot m^{-2}$ (E), and 5.78 $W \cdot m^{-2}$ (F) of UV (280 – 400 nm) radiation with the associated Equation 3.1 for each intensity. Average Hg(0) for three trials is shown as a black line, while error bars (± standard deviation) are shown in grey.

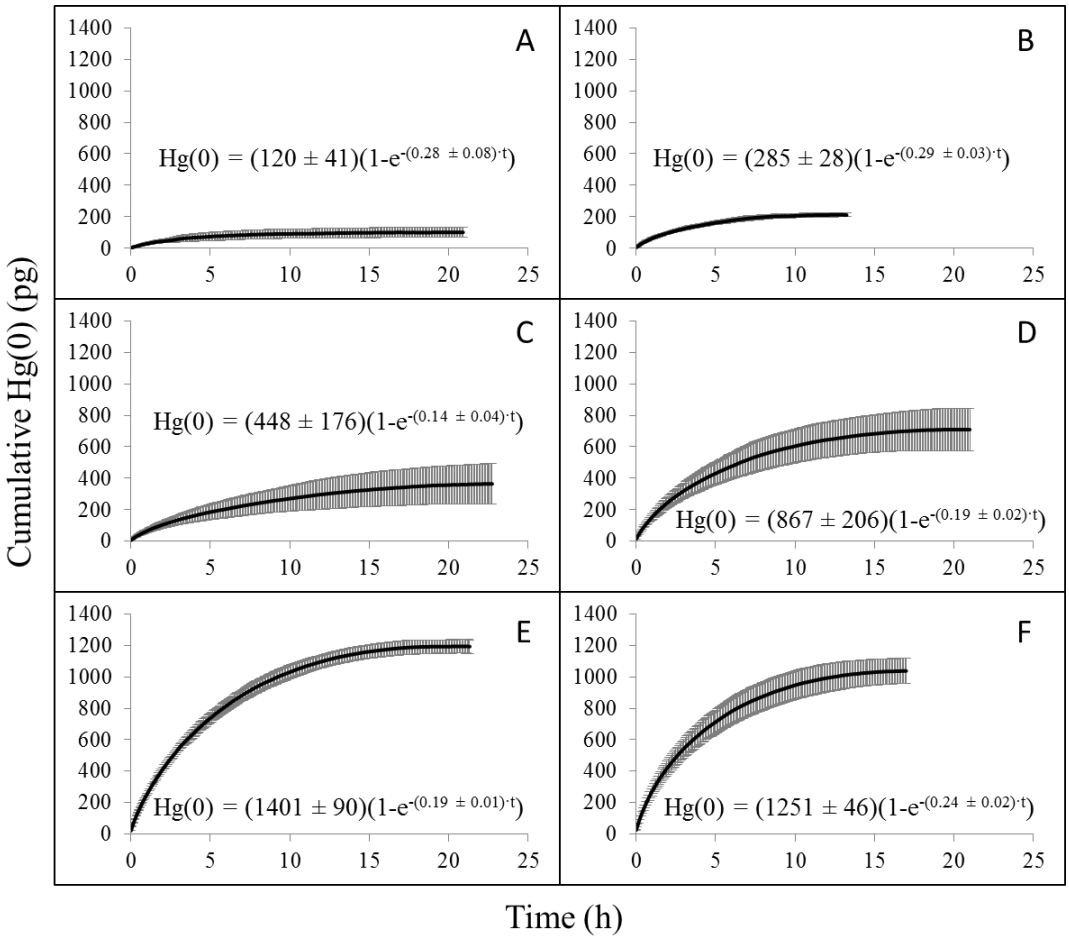

Figure A1.4: Site 3 cumulative Hg(0) collected over the irradiation period for 1.26 $W \cdot m^{-2}$ (A), 1.83 $W \cdot m^{-2}$ (B), 2.39 $W \cdot m^{-2}$ (C), 3.52 $W \cdot m^{-2}$ (D), 4.65 $W \cdot m^{-2}$ (E), and 5.78 $W \cdot m^{-2}$ (F) of UV (280 – 400 nm) radiation with the associated Equation 3.1 for each intensity. Average Hg(0) for three trials is shown as a black line, while error bars (± standard deviation) are shown in grey.

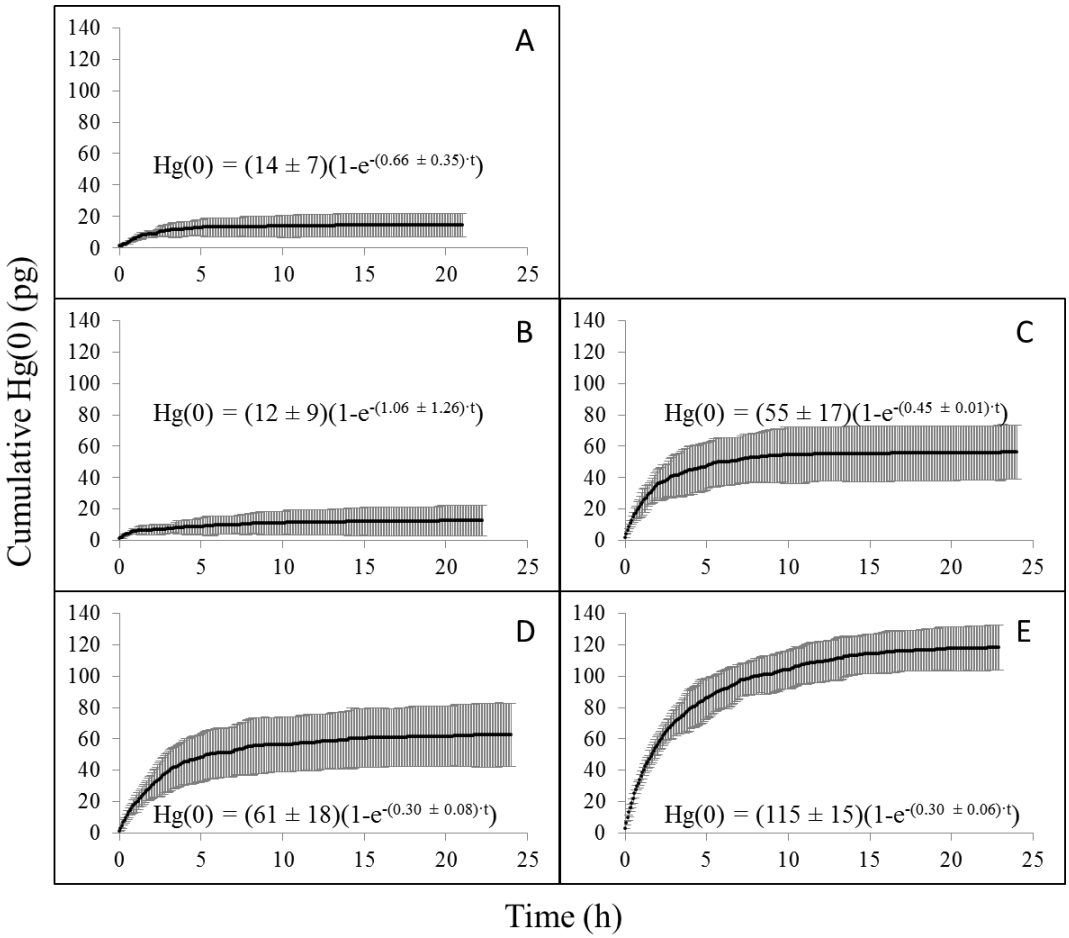

Figure A1.5: Site 1 cumulative Hg(0) in melted snow collected over the irradiation period for 3.52 $W \cdot m^{-2}$ (A), 4.09 $W \cdot m^{-2}$ (B), 4.65 $W \cdot m^{-2}$ (C), 5.22 $W \cdot m^{-2}$ (D), and 5.78 $W \cdot m^{-2}$ (E) of UV (280 – 400 nm) radiation with the associated Equation 3.1 for each intensity. Average Hg(0) for three trials is shown as a black line, while error bars (± standard deviation) are shown in grey. Note that the site 1 melted snow samples were exposed only to higher intensities of UV radiation, since lower intensities did not produce quantifiable levels of Hg(0).

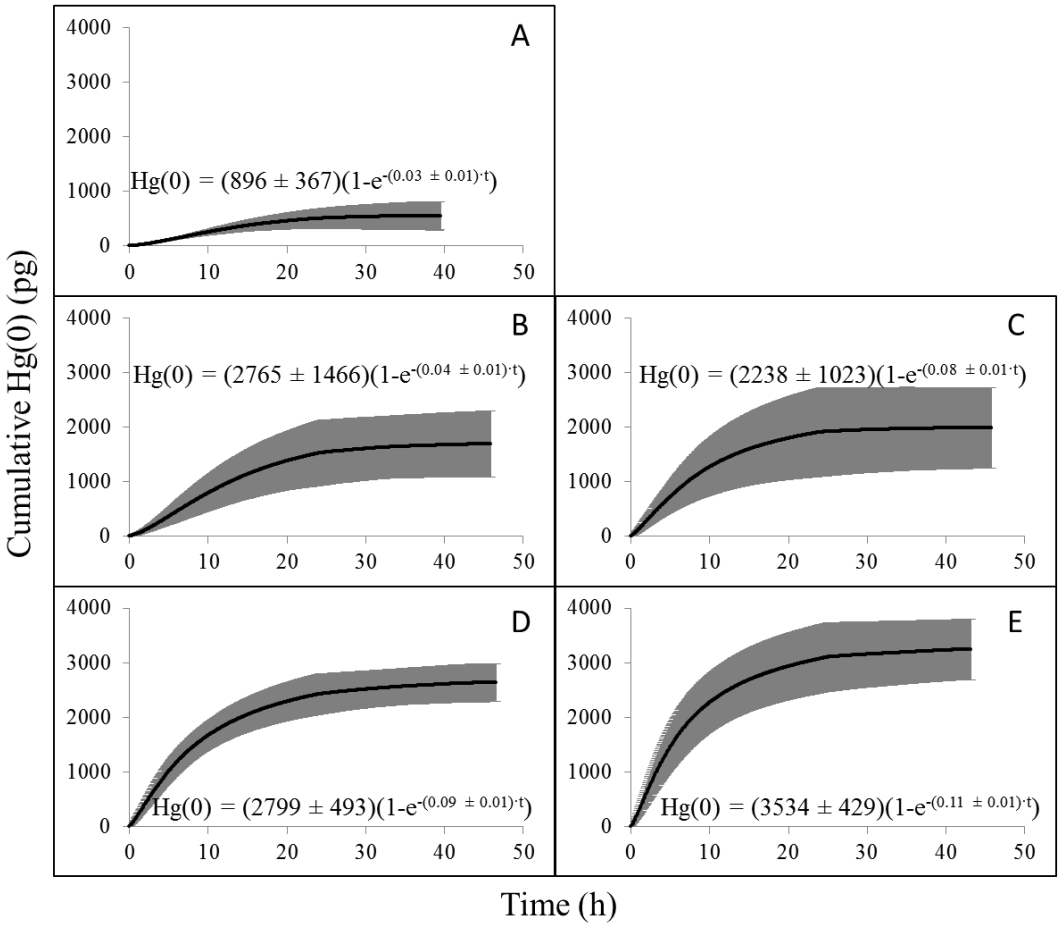

Figure A1.6: Site 2 cumulative Hg(0) in melted snow collected over the irradiation period for 1.26 $W \cdot m^{-2}$ (A), 2.39 $W \cdot m^{-2}$ (B), 3.52 $W \cdot m^{-2}$ (C), 4.65 $W \cdot m^{-2}$ (D), and 5.78 $W \cdot m^{-2}$ (E) of UV (280 – 400 nm) radiation with the associated Equation 3.1 for each intensity. Average Hg(0) for three trials is shown as a black line, while error bars (± standard deviation) are shown in grey.

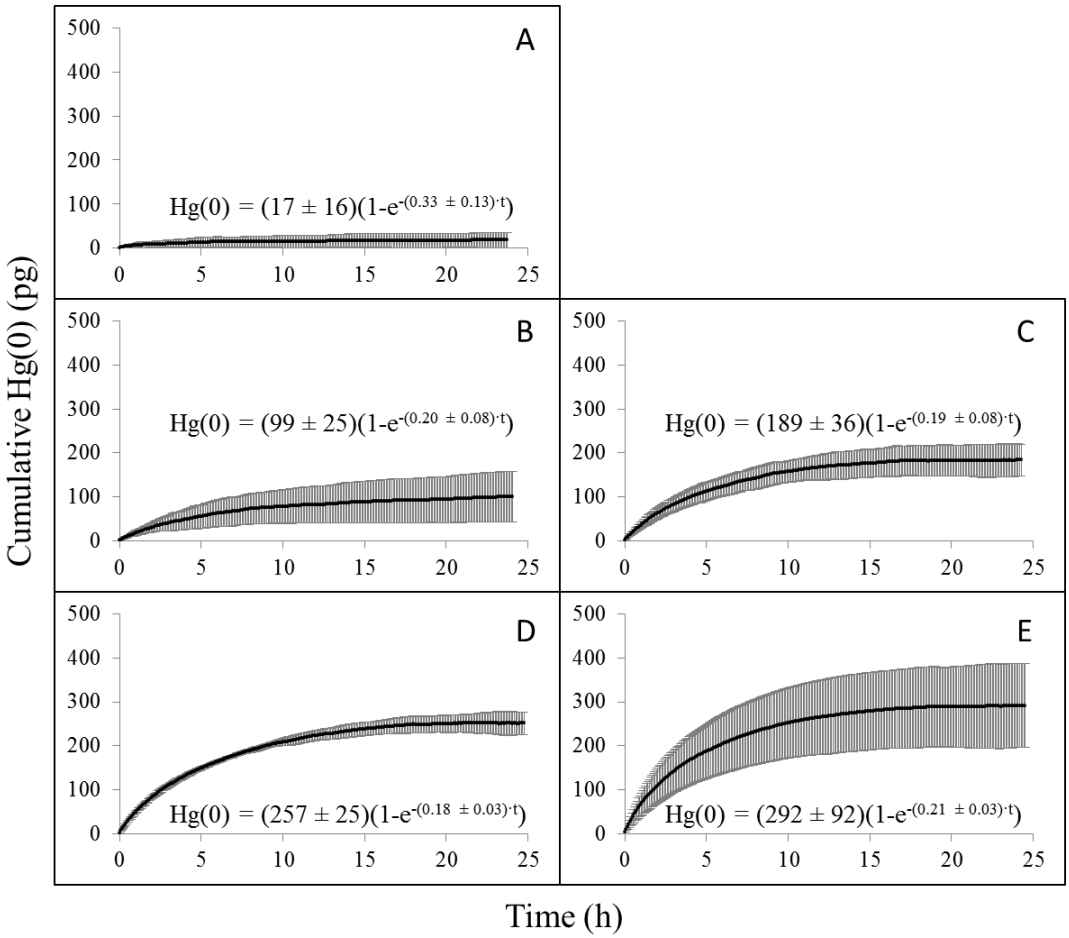

Figure A1.7: Site 3 cumulative Hg(0) in melted snow collected over the irradiation period for 1.26 $W \cdot m^{-2}$ (A), 2.39 $W \cdot m^{-2}$ (B), 3.52 $W \cdot m^{-2}$ (C), 4.65 $W \cdot m^{-2}$ (D), and 5.78 $W \cdot m^{-2}$ (E) of UV (280 – 400 nm) radiation with the associated Equation 3.1 for each intensity. Average Hg(0) for three trials is shown as a black line, while error bars (± standard deviation) are shown in grey.

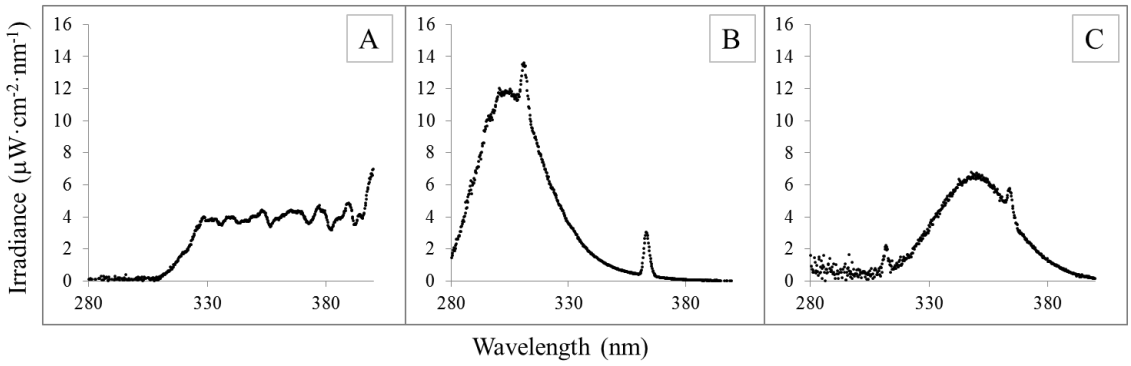

Figure A1.8 UV Spectrum of natural insolation at 1:15 pm, March 10, 2012 (A), 5 UVB bulbs (B) and, 5 UVA bulbs (C) in the LuzChem photoreactor, as measured by an OceanOptics USB 4000 spectraradiometer. UVA bulbs most closely resemble natural insolation spectra, emitting greatest UV intensities from 320 – 400 (UVA) nm, with a small amount in the 280 – 320 (UVB) nm range.

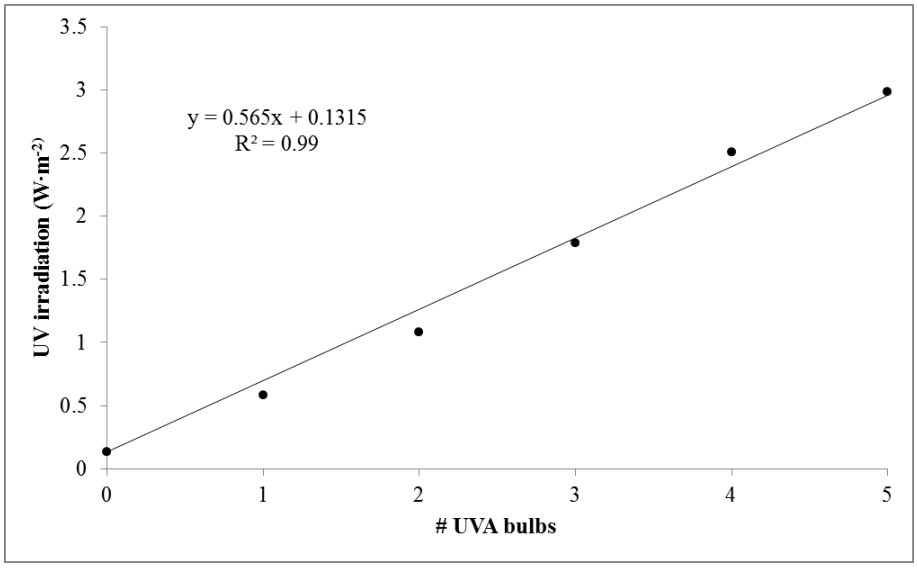

Figure A1.9: UV radiation intensity increases linearly with number of UVA emitting bulbs in the LuzChem photoreactor, as measured by the OceanOptics USB 4000 spectraradiometer.

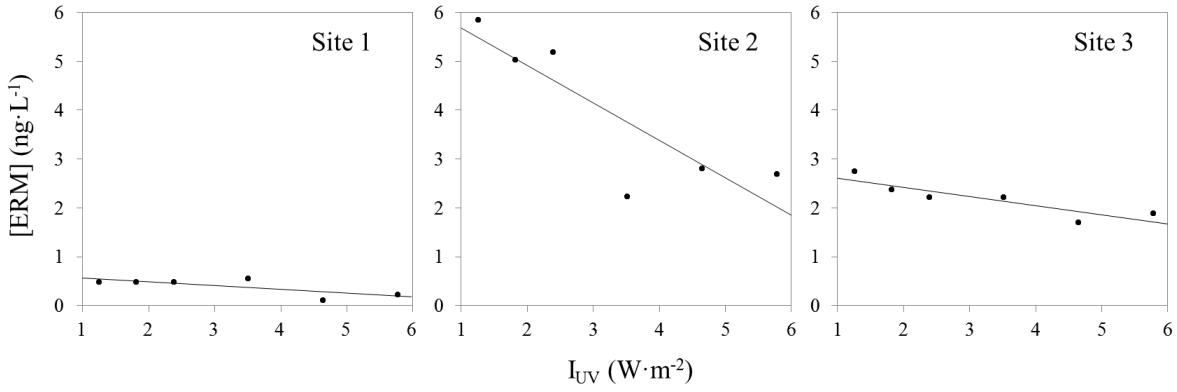

Figure A1.10: Easily reducible mercury (ERM) concentrations in irradiated snow samples from all three sites plotted against the UV intensity of the irradiation. Plots show the linear regression line for [ERM] vs UV intensity for each plot (Equation A1.3); regression data can be found in Table A1.4.

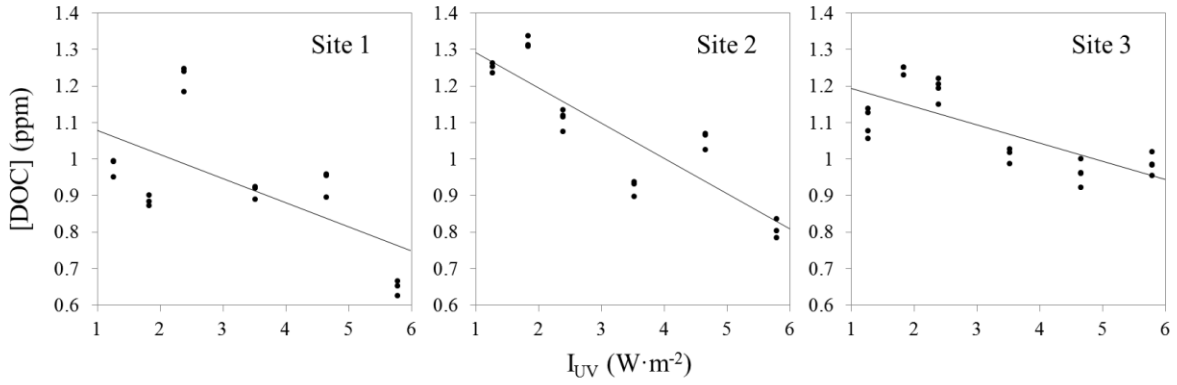

Figure A1.11: Dissolved organic carbon (DOC) concentrations in irradiated snow samples from all three sites plotted against the UV intensity of the irradiation. Plots show the linear regression line for [DOC] vs UV intensity for each plot (Equation A1.4); regression data can be found in Table A1.5. In non-irradiated samples, [DOC] were 1.26,

1.39 and 1.26 ppm for Site 1, 2 and 3 respectively. Overall, with irradiation, 2 – 50% of the initial DOC was lost from the samples.

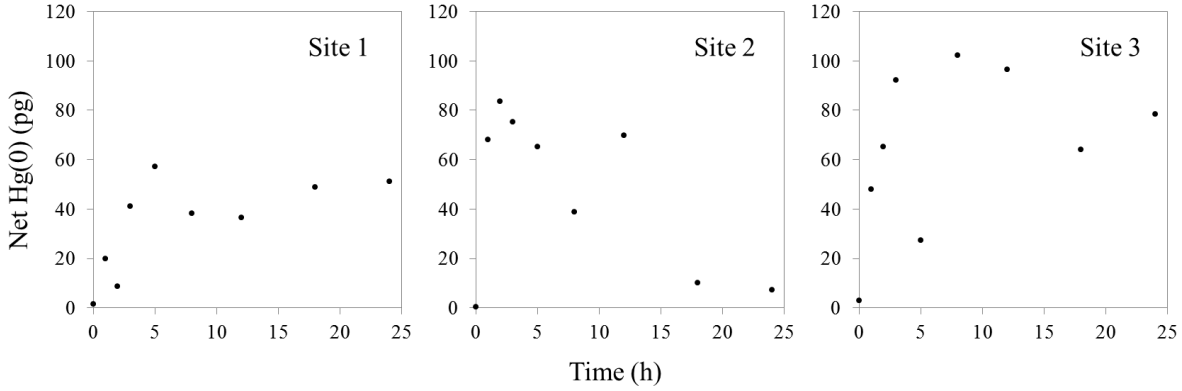

Figure A1.12: Net quantity of Hg(0) produced from irradiation of melted snow from the three sites with 5.78 $W \cdot m^{-2}$ UV radiation.

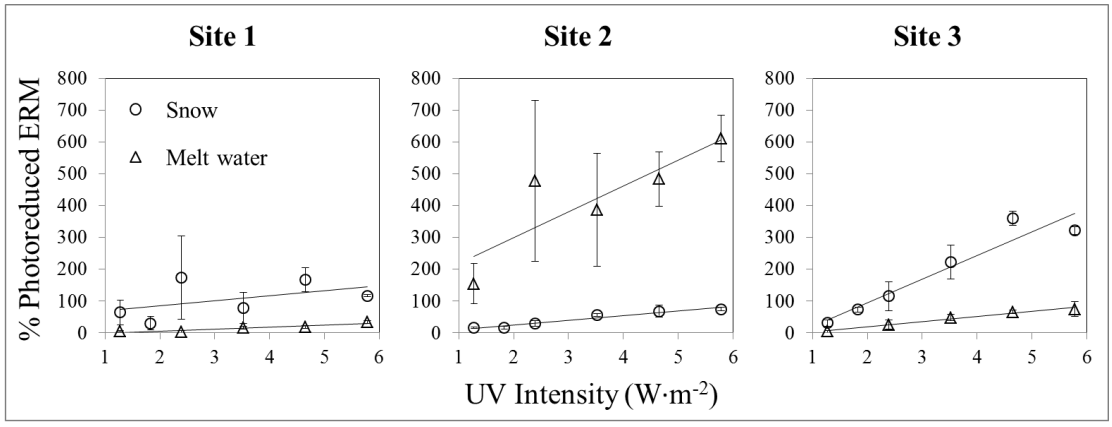

Figure A1.13: Percentage of the easily reducible mercury in a frozen (circle) or melted (triangle) sample that was photoreduced at a given intensity of UV radiation. Each data point is the average of a triplicate measurement, with error bars being plus/minus the standard deviation.

	Site 1	Site 2	Site 3
Sampling date and time	March 12, 2012 10:00 – 10:30 CST	March 9, 2012 12:45 – 13:30 CST	March 8, 2012 10:45 - 12:00 CST
GPS location (Degree/min/sec)	74°41’31 N 094°56’08 W	74°44’13 N 094°56’28 W	74°43’05 N 095°00’16 W
Description	Flat, wind scoured location near an ice covered lake. Very hard packed snow in relatively deep drifts, with no visible rock, overlaid in places by a thin layer of newer windblown snow.	Hilly location with many snow drifts. Deep snowpack, sampled on the lee side of a large hill on the shaded side, with no underlying rock visible. Snow moderately hard and windblown.	Flat, wind scoured location between PCSP base camp and Arctic Ocean (ice covered, no open water); thin hard snow cover with shallow drifts and rocks visible.
Air temperature (°C)	-31.2	-33.3	-38.1
Snow temperature (°C)	-31.0	-35.5	-39.7
Wind speed (km/h)	10.2	8.1	2.6
Relative humidity (%)	100	100	100

Table A1.1: Sampling site descriptions and collected environmental parameters at the time of sampling.

The table below shows the coefficients for Equation A1.1 for each site, with associated standard error (SE) and statistical significance (p) for each term. In Equation A1.1 I_{UV} is the intensity of UV radiation (280 - 400 nm) that the sample is exposed to and k_0 is the pseudo-first order reduction rate constant in the dark

$$k = k_0 + a \cdot I_{UV} + b \cdot I_{UV}^2 \qquad \text{(Equation A1.1)}$$

Site	R^2	p (reg)	k_0	SE(k_0)	p (k_0)	a	SE (a)	p (a)	b	SE (b)	p (b)
1	0.44	< 0.01	0.41	0.10	< 0.01	-0.17	0.07	0.03	0.03	0.01	0.01
2	0.28	0.03	0.76	0.16	< 0.01	-0.30	0.10	0.01	0.04	0.02	< 0.01
3	0.37	0.01	0.45	0.07	< 0.01	-0.15	0.04	< 0.01	0.03	0.01	< 0.01

Table A1.2: coefficients for Figure 3.1, k vs UV intensity curves for frozen snow (Equation A1.1).

The equation for the line fit to these data is below (Equation A1.2), and the constants (with associated standard error, SE, and p-values) for snow from each of the three sites irradiated with UV radiation can be found in Table A1.3. In Equation A1.2 I_{UV} refers to the intensity of UV (280 - 400 nm) radiation the sample is exposed to and $Hg(II)_{red,0}$ refers to the y-intercept, or the total amount of mercury that would be reduced in the dark.

$$Hg(II)_{red} = Hg(II)_{red,0} + a \cdot I_{UV} \quad \text{(Equation A1.2)}$$

Site	R^2	p (reg)	$Hg(II)_{red,0}$	SE ($Hg(II)_{red,0}$)	p ($Hg(II)_{red,0}$)	a	SE (a)	p (a)
1	0.23	0.03	42	39	0.30	26	11	0.03
2	0.83	< 0.01	-12	13	0.35	33	4	< 0.01
3	0.86	< 0.01	-85	39	0.04	112	11	< 0.01

Table A1.3: coefficients for curves fit to $Hg(II)_{red}$ vs UV intensity in frozen snow, with data shown in Figure 3.1 (Equation A1.2).

$$[ERM] = [ERM]_0 + m \cdot I_{UV} \quad \text{(Equation A1.3)}$$

Site	R^2	p (reg)	$[ERM]_0$	SE ($[ERM]_0$)	p ($[ERM]_0$)	n	SE (n)	p (n)
1	0.47	0.08	0.63	0.12	< 0.01	-0.08	0.03	0.08
2	0.66	0.03	6.44	0.84	< 0.01	-0.77	0.23	0.03
3	0.74	0.02	2.79	0.18	< 0.01	-0.19	0.05	0.02

Table A1.4: Coefficients (slope, n, and y-intercept, $[ERM]_0$), with associated error (SE) and statistical significance (p) for the linear regression of [ERM] vs. UV intensity for

irradiated snow from the sample sites. Note that the "p (reg)" term is the p-value for the whole linear regression (Equation A1.3).

$$[DOC] = [DOC]_0 + m \cdot I_{UV} \quad \text{(Equation A1.4)}$$

Site	R^2	p (reg)	$[DOC]_0$	SE ($[DOC]_0$)	p ($[DOC]_0$)	m	SE (m)	p (m)
1	0.23	0.19	1.26	0.15	< 0.01	-0.07	0.04	0.19
2	0.71	0.02	1.39	0.10	< 0.01	-0.10	0.03	0.02
3	0.52	0.06	1.25	0.08	< 0.01	-0.05	0.02	0.06

Table A1.5: Coefficients (slope, m, and y-intercept, $[DOC]_0$), with associated error (SE) and statistical significance (p) for the linear regression of [DOC] vs. UV intensity for irradiated snow from the sample sites. Note that the "p (reg)" term is the p-value for the whole linear regression (Equation A1.4).

$$k = k_0 + a \cdot I_{UV} + b \cdot I_{UV}^2 \quad \text{(Equation A1.5)}$$

$$k = k_0 + a \cdot I_{UV} \quad \text{(Equation A1.6)}$$

Site	R^2	p (reg)	k_0	SE (k_0)	p (k_0)	a	SE (a)	p (a)	b	SE (b)	p (b)
1	0.25	0.08	2.50	1.89	0.21	-0.77	0.83	0.37	0.07	0.09	0.47
2	0.70	< 0.01	0.01	0.01	0.02	0.01	0.002	< 0.01	N/A	N/A	N/A
3	0.35	0.03	0.49	0.09	< 0.01	-0.15	0.06	0.02	0.02	0.01	0.04

Table A1.6: coefficients for Figure 1 k vs UV intensity curves for melted snow (Equation A1.5, A1.6).

$$Hg(II)_{red} = Hg(II)_{red,0} + a \cdot I_{UV} \quad \text{(Equation A1.7)}$$

Site	R^2	p (reg)	$Hg(II)_{red,0}$	SE ($Hg(II)_{red,0}$)	p ($Hg(II)_{red,0}$)	a	SE (a)	p (a)
1	0.80	< 0.01	-154.4	27.7	< 0.01	44.3	5.9	< 0.01
2	0.32	0.02	467.1	613.8	0.46	436.9	159.8	0.02
3	0.75	< 0.01	-28.6	20.3	0.18	34.5	5.3	< 0.01

Table A1.7: coefficients for curves fit to $Hg(II)_{red}$ vs UV intensity in melted snow, with data shown in Figure 3.2 (Equation A1.7).

Analysis	Site 1 snow	Site 2 snow	Site 3 snow	Site 1 MW	Site 2 MW	Site 3 MW
pH	6.31 ± 0.26	4.22 ± 0.09	5.90 ± 0.17	6.20 ± 0.04	4.26 ± 0.07	5.86 ± 0.12
DOM fluorescence	9.61 ± 2.81	7.55 ± 0.74	6.89 ± 0.96	2.24 ± 1.65	3.20 ± 0.69	3.24 ± 0.59
[DOM] (ppm)	0.93 ± 0.17	1.08 ± 0.18	1.08 ± 0.11	0.64 ± 0.05	0.78 ± 0.37	1.08 ± 0.20

Table A1.8: Results for chemical analyses of irradiated frozen (snow) and melted (MW) snow samples, given as average ± standard deviation for all irradiated samples from each site.

Appendix 2: Chapter 4: Mercury loss from Arctic snow is controlled by UV irradiation, temperature, and snow age

A2.1 Field Hg(0) flux from snow

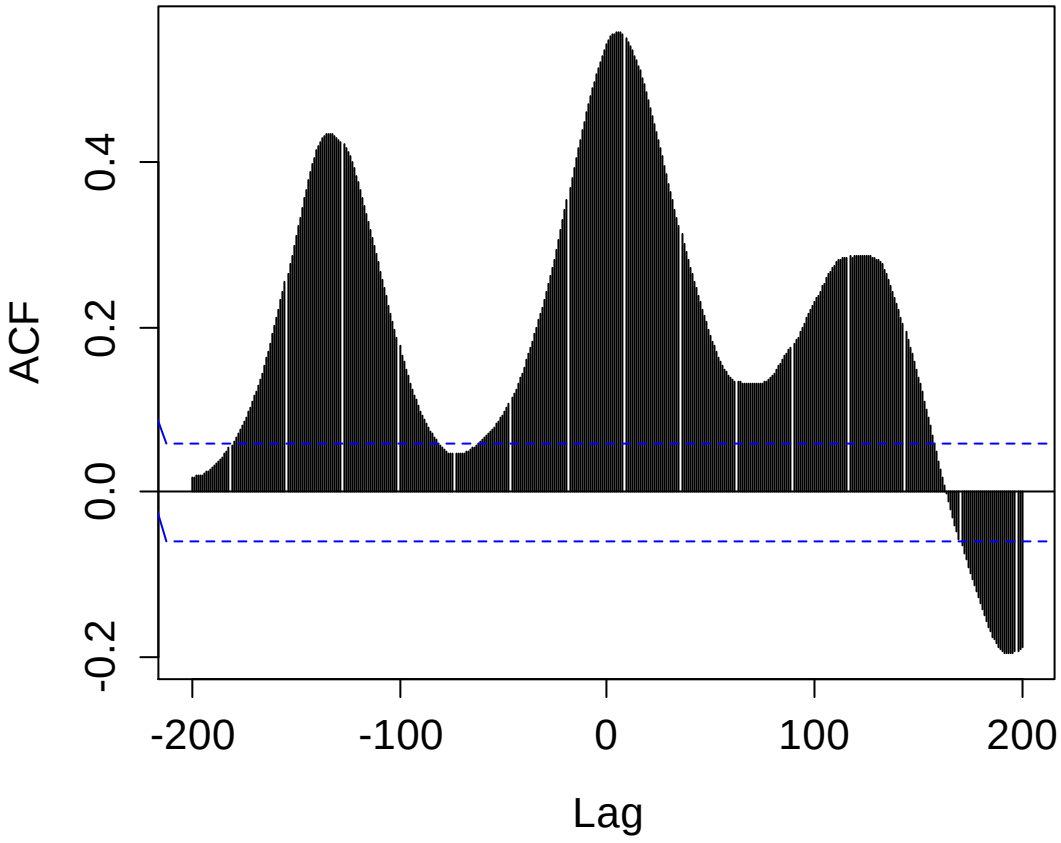

Figure A2.1: Cross correlation analysis of Flux and snow temperature. Each Lag unit represents 5 minutes, since measurements were taken 5 minutes apart. The most significant time lag (maximum ACF) occurs at a lag of 6, which corresponds to a time of 30 minutes. This means that flux lags temperature by ~30 minutes.

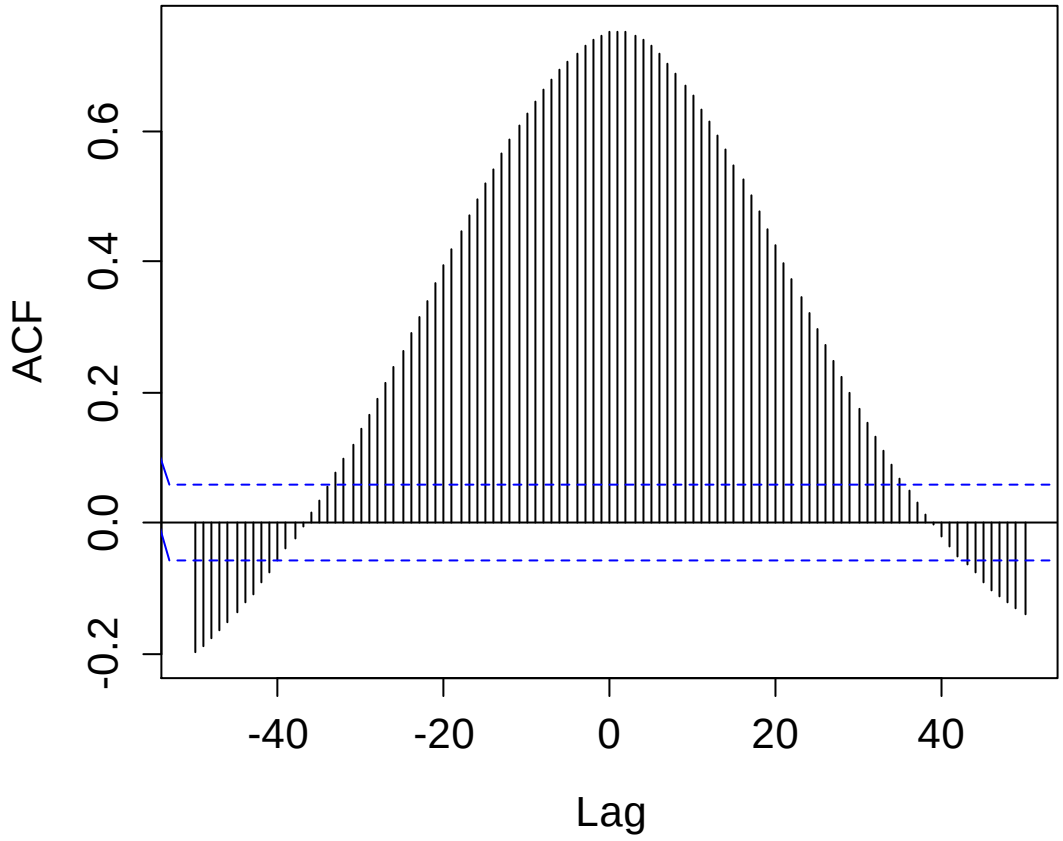

Figure A2.2: Cross correlation analysis of Flux and UV radiation intensity. Each Lag unit represents 5 minutes, since measurements were taken 5 minutes apart. The most significant time lag (maximum ACF) occurs at a lag of 1, which corresponds to a time of 5 minutes. This 5 minute lag time is explained by the time it takes the instrument to quantify Hg(0).

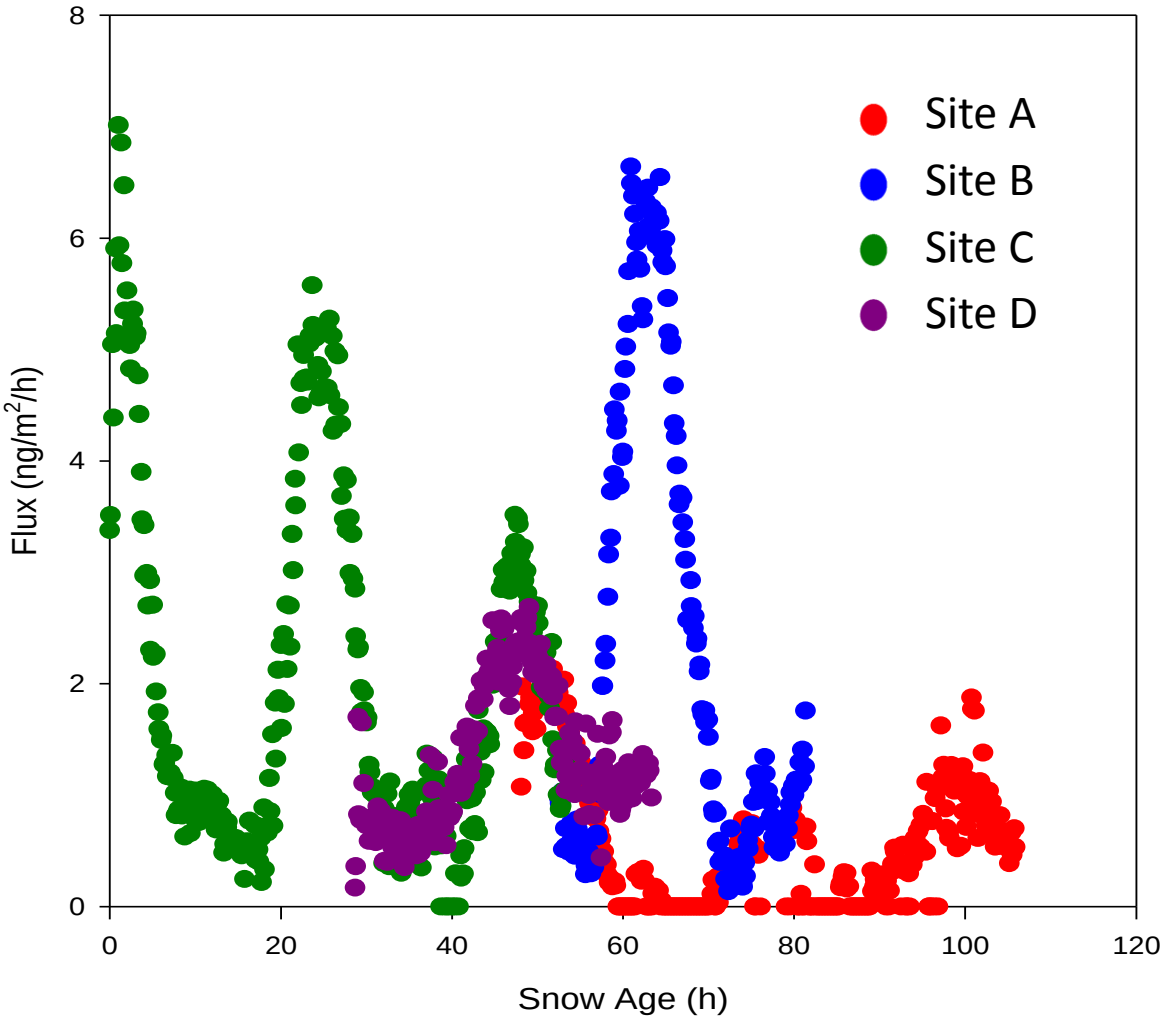

Figure A2.3: Flux of Hg(0) from snow for the 4 snow plots examined, against the age of the snow under the chamber, where snow age represents the time since the last snow fall before the chamber was moved.

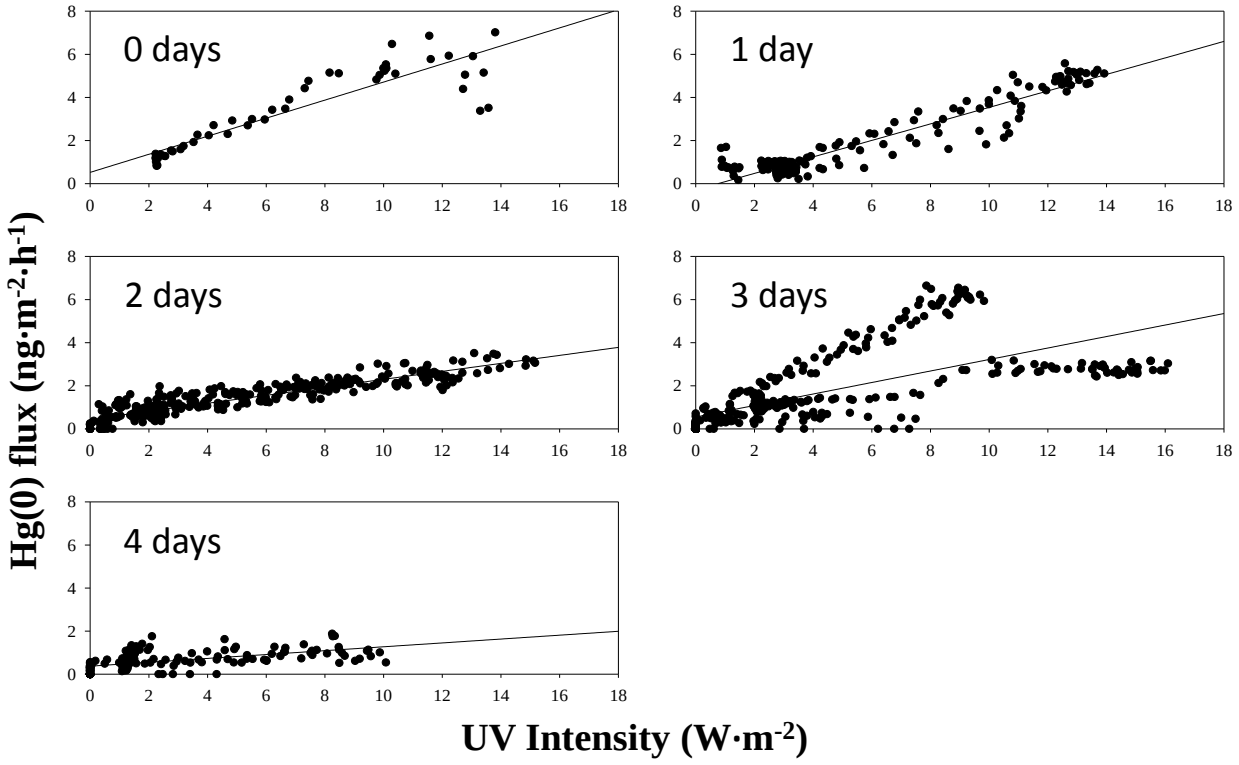

Figure A2.4: Flux of Hg(0) from Arctic snow plotted against UV intensity. Data have been separated based on the age of the snow under the chamber, where snow age is defined as the time since the last snowfall. For 0 days: $R^2 = 0.80$, $p = < 0.01$; for 1 day: $R^2 = 0.90$, $p = < 0.01$; for 2 days: $R^2 = 0.84$, $p = < 0.01$; for 3 days: $R^2 = 0.46$, $p = < 0.01$; for 4 days: $R^2 = 0.33$, $p = < 0.01$.

It should be noted that the length of time the snow has been isolated from atmospheric influence may also be important. In the "3 days" plot the split in data may occur because some data represents snow that has been newly covered with the chamber (top grouping), while the remainder of the data is for snow having been covered >24h. The newly covered "older" snow may have received additional Hg as a result of dry deposition

processes, or the snow may have been perturbed by wind exposing snow that had not previously been exposed to solar radiation.

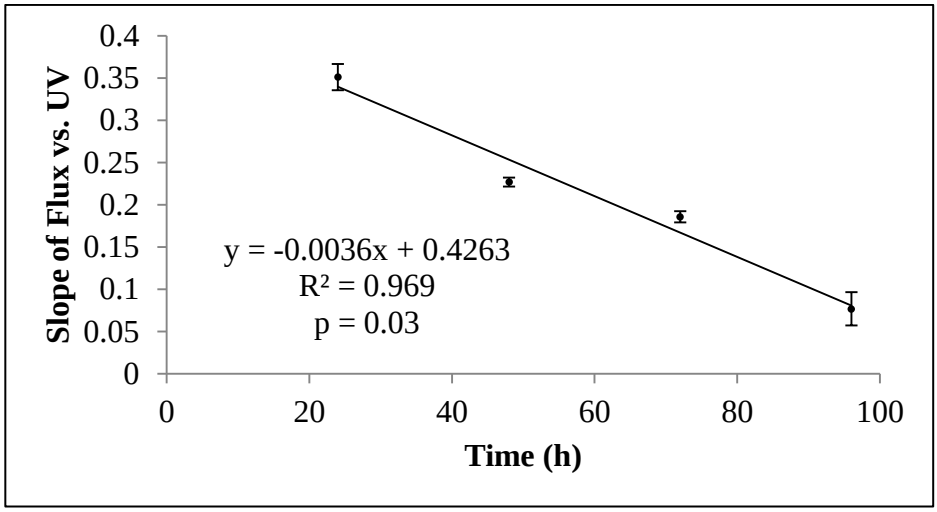

Figure A2.5: Slopes of the lines from Figure A2.1 plotted against time, to determine how long Hg(0) emission from snow covered with a Teflon flux chamber can be expected to occur.

A2.2 Generalised additive model (GAM)

A generalised additive model (GAM) makes use of a number of different variables to describe a given data set. Here we use a GAM to describe flux. Smoothers are the variables we are fitting to the response variable, here (Equation A2.1) the response variable is "Flux" and the smoothers are "Snow.age" and "Snow.Temp". An offset variable is one with a known influence on the response variable, and so the model takes into consideration the influence of the offset on the response variable before determining

the significance of the other variables. The “Flux” results from the GAM, plotted against the measured Hg(0) flux from snow values are seen in Fig. A2.6, and both sets of flux data (measured and modelled) can be found plotted against measurement number in Fig. A2.7, where a measurement was taken every 5 min.

Flux ~ s(Snow.age) + s(Snow.Temp) + offset(UV.Intensity) Equation A2.1

Equation A2.1: Formula of the generalised additive model (GAM) used to determine the significance of temperature and snow age in determining the flux of Hg(0) from Arctic snow. This GAM was run using RStudio Version 0.98.1062.

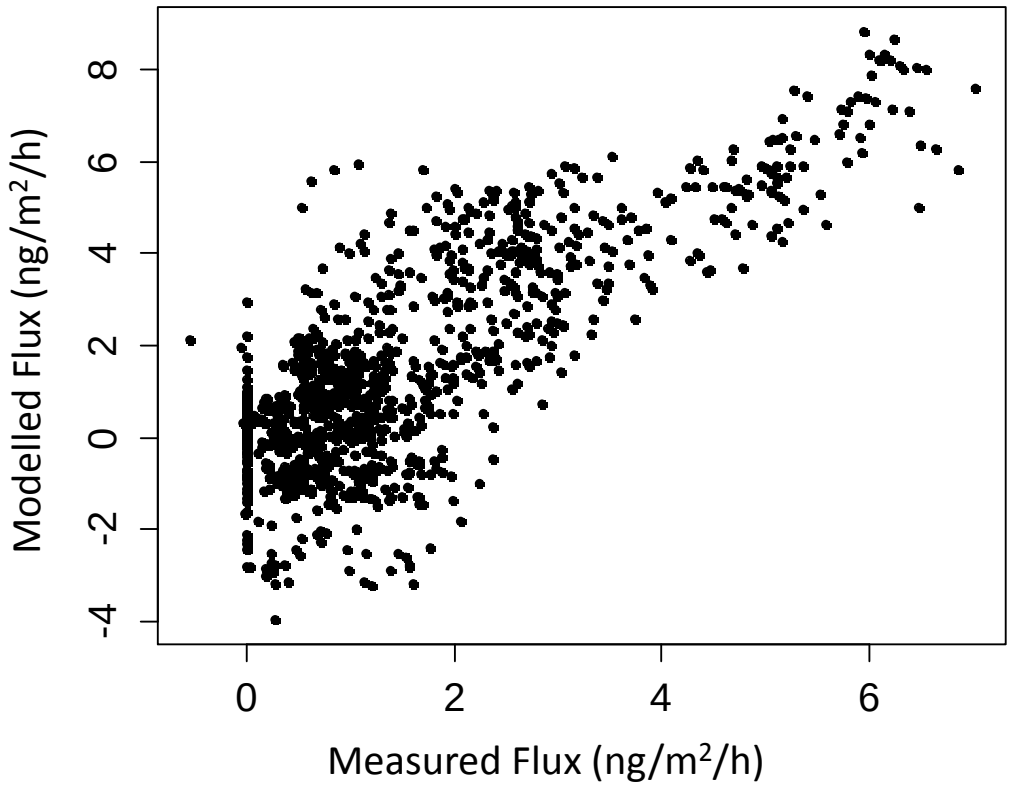

Figure A2.6: The performance of the generalised additive model (GAM), as determined by relating the measured and model fitted Hg(0) flux from snow values. A clear linear relationship is present, and the GAM describes ~77% of the variability observed in the Hg(0) flux measured over the field campaign.

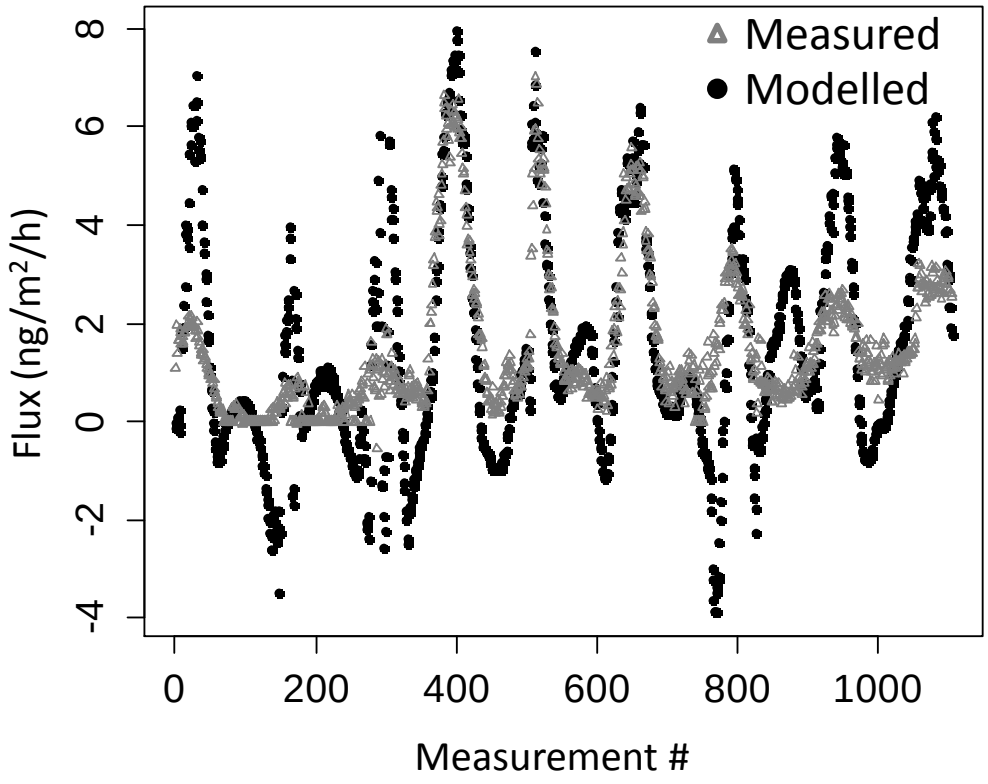

Figure A2.7: Measured and generalised additive model derived Hg(0) flux values for the duration of the campaign. Note that a positive flux represents Hg(0) emission from snow, while a negative flux indicates deposition. A measurement was made every 5 minutes.